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AUGERING AND CORE-DRILLING FOR GEOLOGICAL PURPOSES IN TRINIDAD.*

By E. C. Scott, M.Inst.Pet.

Introduction.

Augering and core-drilling are undertaken to supply information which cannot be obtained from surface exposures and hand-dug pits.

Hand-dug pits have a general depth limit of from 10 to 12 ft., but in the past they have been carried to 15 and 30 ft., in order to get through alluvium and below the weathered zone, which is sometimes very deep in clays and marly clays.

They have the advantage over augering and drilling that each one gives a dip, strike, and a full view of the strata *in situ*, but it should be noted that, where marker beds exist, dip and strike can be obtained by three-point auger work.

Where alluvium or weathered zone is thick, they are of little use and, in addition, weathering of the forams often necessitates going deeper than ordinary pitting permits, even when the clays and shales look comparatively unweathered.

Natural recourse to augering is made when it is required to make examinations below practicable pit depth for foram determinations, position of contacts, etc.

Twenty feet is generally easily obtained with an ordinary carpenter's earth auger (50 or even 100 ft. having been obtained), but in the latter cases it is necessary to employ a tripod and snatch-block for withdrawing the tools. Photos A and B show types of augers commonly employed.

Augering is more particularly applicable to clays, shales, and sandy shale. Soft sands are prone to caving, and hard sandstone and lime cannot be penetrated with economy.

Special augers have been devised to deal with caving and sticky conditions, and have operated with varying degrees of success.

They have included elaborations of the Banka drill, used extensively for alluvial metal examinations, and certain percussion-type instruments have appeared on the market which, it is maintained, can be used to take orientated cores.

All these tools have distinct limitations, principally that most of them require more supervision than can ordinarily be devoted to them in practice.

At depths of over 50 ft. it has been found necessary to employ a light rotary or percussive drill. Percussive drills have not found much favour, and it is possible that, in certain types of country, they offer advantages. Their great objection is that they nearly always demand the use of casing and are not very flexible in application.

The rotary machine has been used almost exclusively in Trinidad, and its use and limitations form the principal part of this paper.

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* Paper presented at a Meeting of the Trinidad Branch held on 22nd March, 1939.

Rotary Machines—Types Used.

The types of rotary machines used fall into four main categories :—

(1) Completely hand-operated.
(2) Hand-rotated with motor-driven pump.
(3) Completely power-driven.
(4) Contra-flush system.

(1) Completely Hand-operated Machines.

With these, the Banka drill and auger might almost be included *sensu stricto*. The usual machine consists of a rotating head with a chuck for gripping the drill-pipe, a feeding device, and a geared assembly for transmitting rotary motion to the drill-rods by means of manual rotation. A hand-operated pump is provided for maintaining flush or circulation round the drill-head.

These machines were the outcome of shallow mining machines, one of which, "the Wombat," was used extensively for military mining purposes during the War.

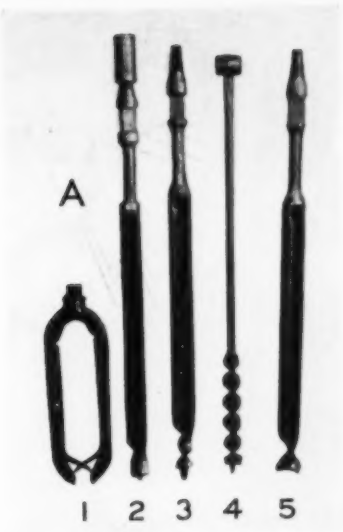
It is almost impossible to supply flush at a rate sufficient to lift cuttings by means of a hand-pump, and therefore the original machines were equipped with an auger-head or core-barrel, in order that excavated material could be removed *en bloc* by withdrawing the tool. The sole function of the flush was then to lubricate the bit and wet the material. Since full circulation could not be maintained, this meant carrying what was essentially a dry hole.

The method will perform quite satisfactorily down to 100 ft., and should show advantage over the auger between 30 and 50 ft., especially as it is possible to obtain cores with a basket-type bit in well-consolidated material.

(2) Hand-rotated Machines with Motor-driven Pump.

When continuous flush is required, as it is in unconsolidated ground, a power-pump is almost essential, and it has been proved by experiments in Trinidad that the rate of drilling is almost entirely controlled by the rate of flush down to 300–400 ft. as the following data show :—

Footage drilled.	Time required.	Manometer pressure.	Amount of fluid circulated per minute.	Remarks.
		(*a*) *With Craelius Pump.*		
10 ft. (100–110 ft.)	38 min.	5 lb. = 70 lb./sq. inch.	9 gals. per minute.	While drilling bit partly got plugged.
10 ft. (110–120 ft.)	40 min.	5 lb. = 70 lb./sq. inch.	10 gals. per minute.	Belt kept slipping.
		(*b*) *With* 6 × 4 × 6 *in. Worthington Steam Pump.*		
10 ft. (120–130 ft.)	12½ min.	10 lb. = 140 lb./sq. inch.	15 gals. per minute.	Installed high-pressure hose.
10 ft. (130–140 ft.)	19 min.	10 lb. = 140 lb./sq. inch.	15 gals. per minute.	—

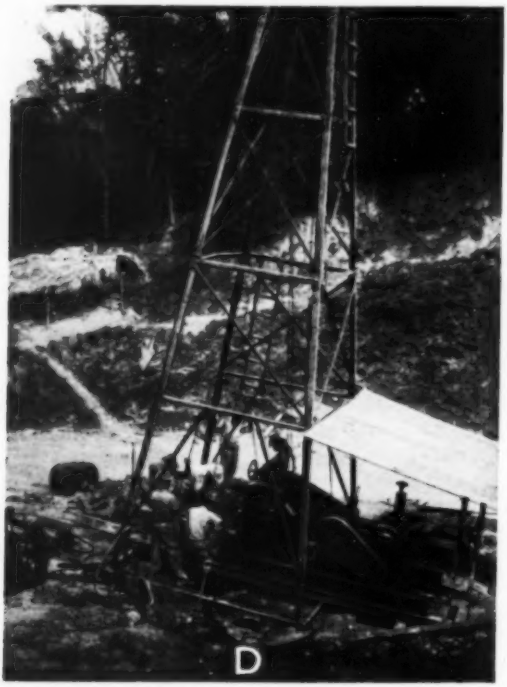


1. Normal 4″ post hole auger.
2, 3 and 5. "Shell" pattern auger for soft formation.
4. 1½″ Carpenter's auger (the most commonly used).

12″ AUGER FOR TAKING LARGE VOLUME SAMPLES AT SHALLOW DEPTH.

[*To face p.* 502.

VIEW OF 1000 FT. CAPACITY DRILLING MACHINE OPERATING IN TRINIDAD.



1000 FT. CAPACITY DRILLING RIG, SHOWING LOCALLY FABRICATED DERRICK DRILLING IN MONE DIABLO QUARRY TRINIDAD.

In other words, down to these depths it takes little or no power to rotate the tools and to withdraw them.

(3) Completely Power-driven Machines.

Originally these were the diamond and shot drills, well known in metal-mining practice and, whilst these were perfectly satisfactory for dealing with hard and semi-hard rocks, a good deal of modification for soft, and particularly for sticky, formations was necessary.

The original diamond drill could use a single-tube core-barrel, *i.e.* the flush passed between the core and the outer single barrel, and also water could be used for circulation, the velocity of which could be maintained, since only a small-diameter hole was necessary.

In soft formations the hole must be plastered with mud and a double-tube core-barrel must be used, since the soft core will not withstand the washing action of the circulation, and sticky ones plug the required annulus.

The double-tube core-barrel must of necessity be of larger outside diameter than the single type; also it has been found that very small-diameter soft cores will not withstand torsional stress, becoming sheared and deformed.

The carrying of the larger hole required for coring and circulation of thick mud introduces another complication—namely, increase in the size of drill-pipe.

Rigs were originally equipped with " A " class rods, and these have been used fairly satisfactorily down to 500–600 ft. However, since the smallest hole that will pass a double-tube core-barrel is 3 in., which gives unsatisfactory cores, it may be accepted as a general principle that " A " class rods are unsatisfactory.

Machines now being ordered are equipped with " N " class rods which permit a 3½-in. or 4-in. hole to be drilled to depths in excess of 2000 ft.

Photos C and D show two views of a 1000 ft. capacity drilling rig, mounted on skids for dragging into locations to which no road exists.

Data concerning these rod sizes are as follows :—

Size.	*E.*	*A.*	*B.*	Old style *N.*	*N* blue.	*N* yellow stripe.	*N* seismo-graph.	*PK.*	*PK* (2½ in.) acme th'd.
O.D., ins.	1⅝	1⅞	1⅞	2½		2½	2½	2½	2½
I.D., ins.	2⅛	1½	1⅝	2		2⅛	2⅛	2⅛	2⅛
I.D. of coupling, ins.	⅝	⅞	¾	1		1⅛	1⅛	1⅛	1⅛
Weight per ft., lb.	2·7	3·3	4·5	4·9		4·9	4·0	8·7	9
Number of joints packed per box	10	6	6	4		4	4	2	2
Gross weight, lb./ft. (boxed):									
For domestic shipment	3·1	3·6	5·2	5·9		5·9	5·4	11·3	11·9
For export shipment	3·2	5·4	5·4	6·2		6·2	6·0	12·3	12·9

Here it may be stated that there is often a hope expressed that these light rigs can be used for production purposes, and it should be clearly understood that drill-pipe sizes, diameter of hole, and depth are all inter-related, as they are in ordinary oil-field drilling.

Producing even a shallow well demands the setting of casing, and the entire equipment of the geological rig is not designed for this. Further-

more, setting 4-in. casing demands a 6-in. hole, and flush velocity has to be increased to limits outside the capacity of pumps if this is to be done.

These rigs will drill large diameter holes, but to smaller depths than their rated capacity for normal holes.

A warning, to those who attempt these large-diameter holes, is perhaps necessary that adequate drill-collar weight should be supplied. Most of the machines (as will be described later) have mechanism for exerting a downward pressure on the cutting tool. If this is done in large-diameter holes, the strain placed on the tool couplings is excessive and in a very short time " twist-offs " will occur.

(4) Contra-flush System.

As the name implies, this system utilizes a reversed flush circulation down the casing and up the drill-pipe. The same principle was adopted in the well-known Fauck system of percussive drilling.

It has three main advantages, viz. :—

(*a*) Since a stuffing-box is necessary to seal off between the drill-pipe and the casing, it is possible to maintain a pressure on the formation.

(*b*) Increased velocity up the drill-pipe assists in removing cuttings.

(*c*) Cuttings are removed directly from the bottom, and a good record is obtained when the formation is suitable.

The application of the method is, however, limited. A seal on the surface casing must be obtained, or flush will break out round it and this is liable to occur when no casing seat is available. Furthermore, when porous formations are encountered, fluid will be lost, due to the increased pressure which must be applied to them in order to obtain circulation.

A novel three-plunger slush-pump is used, and is driven off the drilling engine through a gear-box.

It is claimed that over 2000 ft. can be drilled with a machine of this type, weighing 5100 lb.

The system is obviously mainly applicable to dense well-consolidated rocks.

Description of Machines.

(1) *Mountings.*

In designing, the prospecting drill manufacturers have to fulfil exacting requirements of portability, and have, to date, concentrated on two main mountings :—

(*a*) Truck or tractor.

(*b*) Skid.

Whilst the original diamond drill was almost always skid-mounted, as it had to operate on locations over dams, down mines, etc., the modern oil country equivalent has been preponderantly truck- or tractor-mounted.

Whilst truck-mounting is eminently satisfactory for open flat country with moderate rainfall, it is useless in Trinidad, with its maturely eroded peneplanation, forests, and high rainfall.

Tractor-mountings have some advantages, but they have not been employed as yet, due to :—

(*a*) The difficulty of getting them over public roads. (This disadvantage has now been modified by the invention of the rubber track.)

(*b*) Costly bridges and fillings would be required in hilly country.

(*c*) The cost of clearing forest for a tractor and the royalty to be paid are both excessive.

(*d*) The initial cost of the machine is much greater.

Skid-mountings are normally used in Trinidad, and the smaller machines are towed to the location by bulls. Some attempts have been made to drag machines by their own winch-power, but gear ratios are not at present designed for this, and the skid-beds are not given a sufficient upward curve to permit of easy riding over uneven ground. Altogether, this subject has not been closely studied by manufacturers, probably because the wider demands for truck-mounted units, due to seismology requirements as well as those of geology, in flat countries heavily covered by alluvium have kept them fully employed.

In transporting the present skid-mounted units by means of their own power, it has been found essential to make use of a cat-head, and not of the clutch and wire line used for rod-hoisting, since, if the latter is used, clutch linings burn out very rapidly.

A recent design which equips the pump-engine with a pulling-winch has much to recommend it.

(2) *Drive.*

As has already been stated, the machines are usually of the type which permits a downward pressure to be exerted. Thus, a Kelly or drill-stem is generally dispensed with, and the drill-pipe is gripped in a chuck, the down pressure being supplied either by a ratchet and spur-wheel or by hydraulic cylinders. One medium-depth machine uses a Kelly, and the downward motion is obtained from tandem wire-lines operated from the hoisting-drum and attached at the other end to eyes in the swivel.

The immediate reaction is towards the Kelly type of machine, because of its similarity to the normal oil-field rotary and because it provides a spudding device, but there is no doubt that the facility of the hydraulic rams has much to recommend it, as it provides, besides emphatic down pressure, upward lift, which can be used to free jammed piping and to alleviate the load which must otherwise be thrown on an admittedly light derrick.

(3) *Engines.*

Engine-power for the light rigs is produced from gasoline motors.

With cheap fuel available, it has been the principle to sacrifice engine size and efficiency for uniformity. Thus, on the 1000-ft. machine, 20-h.p. motors have been used on both the pump and draw-works engines, although considerably less than 20 h.p. would be satisfactory for the draw-works.

In line with this desire for uniformity is the practice of some manufacturers to use standard mass-produced car engines, since a local supply of spare parts for these is generally available.

The weight of the power units can be somewhat cut if they are inter-

connected with clutches and chain or Tex-rope drives, and, furthermore, this principle permits of a rig being increased in power in order to add to its depth capacity, although there is obviously a limit to the practicability of the scheme.

(4) *Cutting-tools.*

The normal cutting-tools used in soft formations are the fishtail bit and soft-formation core-barrel.

For hard formations the diamond-set single-tube core-barrel is used almost exclusively in Trinidad, but medium-hard formations, such as limestone, can be successfully drilled with borum-tipped saw-toothed crowns.

Diamond bits are a very expensive item, and in other countries are being replaced by the rock-bit, Calyx shot, and weld-set diamond-head in medium-hard ground.

At present the rock-bit is not made in sizes below 4 in., and in any case it does not provide a core in this small size.

Calyx shot are satisfactory only in ground which is continuously hard. If there are any appreciable soft layers, the shot are side-tracked into the formation and lost.

The weld-set diamond bit is a new innovation; it is much cheaper than the normal hand-set article, since it is more quickly made and smaller stones may be used.

It would be surprising if this article did not eventually provide a solution for some hard-rock drilling encountered with big oil-field rigs.

Methods and Scope of Work.

Apart from its almost universal application to seismic work, the geological rig is being used with increasing frequency to aid surface examinations. Not only are normal contacts checked by sections and groups of holes, but also the hade and throw of faults are ascertained.

During the last few years, co-operation with Messrs. Schlumberger has provided a service whereby coring can be cut out when examining contacts of porous with non-porous rocks. In Trinidad this has been particularly useful, since faults play a major part in oil accumulation.

Another most important rôle of the geological drill is to check and elaborate stratigraphical sequences at type localities. So many type-sections in Trinidad are confused by epidiapiric influences, mud-flows, and other complex conditions, that this service is of great value.

It has been found economical to operate two or more small machines together, information being thereby more rapidly to hand and supervision and distribution of labour easier. The method at present adopted is to use three crews for two rigs. Thus, all three can be employed on one rig for continuous work if conditions demand it.

As a general principle, it is accepted that a number of shallow holes are preferable to one or two deep holes for dealing with specific problems.

As regards scope, these machines are obviously designed to fill the gap between normal surface surveys and exploration drilling proper.

The limit of a light portable outfit is about 1200 ft., although a tendency

is now manifest to copy the multiple-engined diesel rigs, and so make them light rigs capable of additional depth without increasing the weight of components.

Some truck- and tractor-mounted units are capable of between 2000 and 3500 ft., but the latter depth is obviously encroaching on the duties of a normal oil-field rig.

The normal sequence of exploration is suggested as being :—

(1) Surface and/or geophysical surveys.
(2) Confirmation drilling with geological outfits.
(3) Testing to depth with normal rigs.
(4) Full testing for production.

This paper would not be complete without some mention of recent developments under (3), known as slim-hole drilling.

There is obviously a gap between the 1000–2000 ft. potential of the prospecting drill and the heavy 5000–10,000 ft. rigs used for normal oil exploitation, and experiments have produced the small-hole practices now reported from the United States of America.

These latter practices call for a rig as heavy as that used for exploitation, but it is maintained that very appreciable savings can be made in casing, speed, and wear of equipment, but that weight cannot be much reduced is due to the fact that pump pressures increase in small holes. Heavily powered big pumps are therefore still required, and these largely control the weight of the rig.

Most of these slim-hole outfits are capable of from 6000 to 8000 ft. with 3- to 4-in. drill pipe. The gap therefore still exists, and in all probability the companies involved in considerable exploration programmes would be well advised to equip themselves with a rig which would operate economically with 4½-in. drill-pipe down to 3500 ft., and might be used to 5000 ft. with smaller sizes. Much will be possible along these lines when operators cease their demands for a pump which will provide big volume but which can be converted by the use of liners to provide high pressure and small volume.

The technique of slim-hole drilling to considerable depths must obviously be dependant on local conditions, but already sufficient experiment has been made in Trinidad to warrant the assertion that worth-while savings are possible by reducing the diameter of exploration holes where the terrain does not demand the setting of an abnormal number of strings of casing.

The author wishes to express his thanks to Mr. Trafford and Mr. Laidlaw for information given, and to Trinidad Leaseholds, Ltd., for permission to read the paper.

DISCUSSION.

In opening the discussion the author said that since the paper was a rather bare recital of facts, he would ask the Chairman's permission to digress from normal procedure and to initiate an informal debate on two subjects which were connected with exploration drilling in Trinidad, namely,

1. The abnormal pressure gradients encountered in Trinidad oilsands which were such that very heavy mud had to be used in drilling.

In normal oilfield practice it could be assumed that if a certain weight mud would deal with the pressure in an upper oilsand, it would also be satisfactory for one lower down.

In Trinidad, however, abnormal pressure sands are frequently encountered and geologists were invited to comment and suggest explanations.

2. There had been suggestions in current literature to the effect that—" since the probability of finding oil in an exploration well was in excess of 1 in 10; in general it would be economic to drill such wells with the object of obtaining information only, and to forgo any possibility of producing them if oil were encountered."

Discussion on the value locally of such practices was suggested, and in addition members were asked to consider whether it would not be possible to design a rig to drill a small hole to a considerable depth (4000 ft.) using light equipment which would not call for the building of a heavy duty road.

An absorbing discussion took place on the lines suggested by the author, in which Messrs. Harris, White, Bushe, Porter, Kugler, Halse, Fletcher, and Suter took part.

It was agreed that the reason for formation-pressure anomalies in Trinidad oil-sands was not clearly understood. Compression of competent members in the cores of anticlines and similar phenomena related to epidiapiric folding have probably played their parts, as may also wholesale *décollement* of blocks of soft strata from the continental shelves. It was noted, however, that, oil concentration being undoubtedly connected with faulting, it was difficult to reconcile a theory of upward migration with many of the observed pressure anomalies.

Other suggestions mentioned as possible solutions were periods of erosion after compaction of successive zones and varying polymerization changes of the oil within different sands.

Regarding the scope of so-called slim-hole drilling, it was admitted that abnormal formation pressures and the incidence of caving formations, as common occurrences in Trinidad, curtail to some degree the extent to which this can be practised. Some interesting figures, however, were given which indicated a growing tendency to drill smaller holes for production purposes as well as for exploration wells.

It was generally agreed that an appreciable saving could be made in the total cost of exploration drilling on a large scale by adopting slim-hole methods. It was assumed that slim-hole would prevent, or at any rate restrict, the possibilities of producing a well drilled on these principles, and they could not therefore be deemed to apply to outstepping or " semi-exploration " wells on producing fields.

The suggestion that it should be possible materially to reduce the weight of machinery necessary to drill small-diameter holes to a given depth was fully discussed, and the general consensus of opinion was that a machine had not yet been designed which could be transported into the forest and serviced there without the facility of a road.

It was felt that, once a road was admitted as being necessary, the small curtailments in machinery weight which were possible would not be justified, as they would sacrifice the efficiency.

Thus, it appears that, whilst very appreciable saving in casing, bits, time, fuel, etc., may be visualized by the proper employment of slim-hole drilling, at present machinery weight and roads must remain essentially as required for a normal rig to depths over 6000 ft.

A further discussion developed on the possibility of adapting steam power to furnish more mobile rigs, and it was pointed out that water-tube boilers of increased pressure, poppet valve-engines, and single-acting three-throw pumps were all possible solutions to the weight problems where adequate fuel and water were available.

THE MEASUREMENT OF THE FLOW PROPERTIES OF BITUMENS.*

By D. C. Broome, F.C.S., M.Am.Chem.Soc., F.Inst.Pet.

Introduction.

The flow properties of bitumens have always been regarded as of considerable importance and, ever since laboratory testing of such substances has been employed, the tests carried out have included various forms of flow measurement. Originally, these tests were confined to direct measurement of flow by such instruments as the Redwood or Engler viscometers and measurement of the "hardness" or "consistency" by means of the penetrometer. The latter test in particular was found to be very useful as a factory control test, but with the development of the asphalt and bitumen industry other methods were evolved to give a wider and truer picture of the flow properties of the materials employed. Thus the following tests, amongst others, are now extensively employed for routine purposes in this country, in addition to those already mentioned :—

(1) Softening-point tests by Ring and Ball [1] or by Kramer–Sarnow method.[2]
(2) Twisting-point test.[3]
(3) Float test.[4]
(4) Fraass brittle point.[5]
(5) Ductility.[6]

All these, however, suffer from certain disadvantages, and in particular they are inadequate for providing the information required for a full understanding of the properties of the materials employed, in that the majority of the tests give no information as to the properties of the materials *at the temperature at which they will exist on the road*. The principal exceptions to this are the penetration and ductility tests, but even here the information obtained is very inadequate, as the tests are normally carried out at one temperature only. With the majority of bitumens, the ductility test at 25° C.—as normally specified—gives results of "plus 100." The actual ductility may be 200, and it may be 500, but with the limited scope of the standard machine there is no means of telling. The situation, with all the above-mentioned routine tests, is still further complicated by the fact that very few bitumens employed in this country are true fluids. This means that :—

(*a*) it is difficult to compare results obtained by one method with those obtained by another;
(*b*) it is difficult to express the results of any tests in terms of absolute units;
(*c*) it is generally not possible to extrapolate consistency/temperature curves—*e.g.*, to give data for lower temperatures.

* Paper presented to a Meeting of the Asphaltic Bitumen Group of the Institute of Petroleum on 28th March, 1939.

In addition, it is important to determine the extent to which a bitumen deviates from the laws of true fluids, as if, for example, a road is made with a bitumen which is a true fluid, this will tend to displace even under the slightest stress. On the other hand, if the bitumen is at all plastic, it offers a definite resistance to displacement, and the greater the degree of plasticity the greater will be the force necessary to displace the bitumen. In other words, the higher the " degree of plasticity," the less tendency there will be for a road constructed with that bitumen to suffer from deformation. For the sake of simplicity at this stage, the term " plasticity " is used here to express that property which enables a material to be moulded; and the term " degree of plasticity " to indicate the extent to which a material deviates from being a true fluid. As this property will be referred to again later in this paper, it may perhaps be wise to bear in mind the more scientific definition proposed by Bingham : [7] " If, in non-turbulent flow, the ratio of flow to force is constant, the material is said to be fluid; otherwise it is plastic."

A considerable amount can be done by making fuller use of the routine apparatus. For example, all the tests can, and should be carried out over the widest possible temperature range. This gives most useful data, particularly with the ductility test, as, when ductility/temperature curves are plotted, these are usually found to be of the general form shown in Fig. 1. For example, test at 25° C. only tends to indicate that Sample C is much better than Sample B, whereas if the temperature is increased somewhat, the situation is reversed. In fact, Sample B would be much better in practice than Sample C. In the same way, tests should be carried out over a range of temperature with other apparatus.

It has been suggested by Thelen [8] that the flow properties of bitumens can be evaluated in terms of absolute viscosity by obtaining a series of successive penetrations without touching either the sample or the needle. This method was modified by Rhodes and Volkman [9] and further studied by Traxler and Moffatt.[10] The viscosity may be calculated according to this method in accordance with the equation :—

$$V = \frac{M \times D^t \times 1{\cdot}25 \times 10^7}{(P_f + P_i - 46)(P_f - P_i)}$$

where V = viscosity in poises,
P_f = final penetration in decimillimetres,
P_i = initial penetration in decimillimetres,
D_t = time interval in seconds,
M = mass in grams of load on the needle.

The average shearing stress at the surface of the needle and the corresponding rate of shear may be evaluated as follows :—

$$\text{Shearing Stress, } F = \frac{0{\cdot}6243M \times 10^6}{(P_f + P_i - 46)}$$

$$\text{Rate of Shear } \frac{dv}{dr} = \frac{0{\cdot}4999(P_f - P_i)}{D_t}$$

This is interesting, but, as shown by Traxler and Moffatt, the most essentially viscous asphalts give rheological diagrams by this method

indicating negative yield stresses. This shows that the test as now used is not on a sound theoretical basis. It is, however, of some help in the study of certain problems, such as the age-hardening of bitumens, since a number of tests may be performed on a single sample of hard bitumen without appreciably disturbing it.

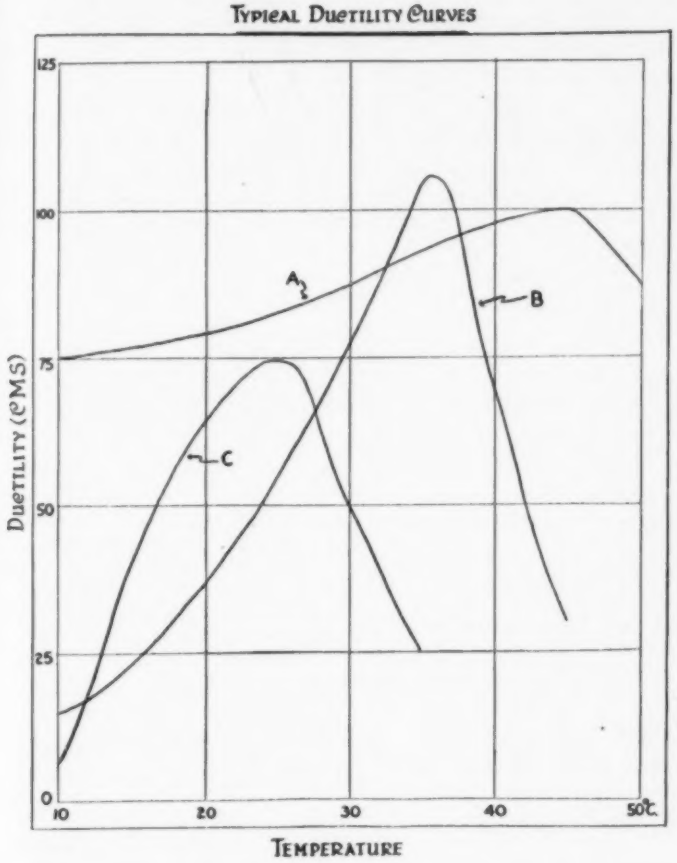


Fig. 1.

Modification of Routine Apparatus.

Still more information can be obtained by simple modifications of existing routine apparatus. One of the best examples of this is the adaptation of the original Frankland Taylor twisting-point apparatus [3] as an absolute viscometer [11] by the use of a cylindrical specimen with square ends to fit into the cups of the standard apparatus. If the temperature is kept constant

throughout the test, the viscosity may readily be calculated by means of the equation :—

$$V = \frac{mgrlt}{1000\pi^2 R^4}$$

where V = viscosity in kilopoises,
m = mass of weight used to apply torque,
g = acceleration due to gravity,
r = radius of torque drum plus card,
l = length of sample,
t = time per revolution (secs.),
R = radius of sample.

With this modification a detailed study of the flow properties of many bitumens can be carried out by performing the test at various temperatures, and with various loads. Normally, this test is suitable only for materials having a viscosity at the test temperature of $1–40 \times 10^3$ kilopoises—*i.e.*, of approximately 15–75 penetration.

Some typical examples of viscosities obtained with this apparatus are shown in Table I :—

TABLE I.

Typical Viscosities with Twisting-Cylinder Viscometer at 25° C.

Bitumen.	Penetration.	Viscosity kilopoises.
Asphaltic Bitumen—Mexican Crude	61	5,499
Asphaltic Bitumen—Venezuelan Crude	59	1,310
Asphaltic Bitumen—Panuco Crude	68	3,582
Refined Trinidad Lake Asphalt 50% * / Asphaltic Bitumen 200 Pen. (Panuco Crude) 50%	44	17,512
Refined Trinidad Lake Asphalt 85% / Liquid Flux "A" 15%	33	14,328
Refined Trinidad Lake Asphalt 83% / Liquid Flux "B" 17%	36	7,959

* Proportions by weight.

These figures indicate clearly that, quite apart from the more scientific nature of such an absolute viscosity determination, the latter is a much more sensitive test than the penetration.

The apparatus in its modified form has two further advantages. Firstly, it may be used to determine the "degree of plasticity," and secondly for elastic recovery measurements. For the former, reference should be made to some work by Saal and Koens,[12] who found that the viscosity of a bitumen may be calculated from the penetration, thus :—

$$V = \frac{5{\cdot}13 \times 10^6}{(\text{penetration})\ 1{\cdot}93}$$

This is applicable only to those bitumens which are true fluids, but if the penetration and absolute viscosity are determined experimentally, the per-

centage difference between the observed and calculated viscosity will be a measure of the degree of plasticity of the material, thus :—

$$\text{Degree of Plasticity} = \frac{(V \text{ obs.} - V \text{ calc.}) \times 100}{V \text{ obs.}}$$

A few typical figures are given in Table II :—

TABLE II.

Typical Plasticity Figures at 25° C.

Bitumen.	Penetration.	Plasticity.
Asphaltic Bitumen—S. Mexican Crude	61	33·8%
Asphaltic Bitumen—Panuco Crude	68	58·9%
Asphaltic Bitumen—Venezuelan Crude	59	8·4%
Asphaltic Bitumen—Texas Crude	59	12·3%
Trinidad Lake Asphalt 50% / 200 Pen. Bitumen (Panuco). 50%	44	79·8%
Trinidad Lake Asphalt 50% / 200 Pen. Bitumen (Venezuelan) 50%	39	18·8%
Trinidad Lake Asphalt 50% / 300 Pen. Bitumen (Panuco). 50%	49	81·8%
Trinidad Lake Asphalt 50% / 500 Pen. Bitumen (Panuco). 50%	65	81·2%
Trinidad Lake Asphalt 85·5% / Trinidad Flux 14·5%	44	72·8%
Trinidad Lake Asphalt 83% / Trinflux 17%	43	53·5%
Trinidad Lake Asphalt 80% / Texaco Flux 20%	26	80·5%
Asphaltic Bitumen (Lobitos Crude) 60% / Trinidad Lake Asphalt 40%	31	67·4%

Another useful modification of existing apparatus consists in carrying out ductility tests at varying speeds. By this means the very high ductility materials may be made to give figures well within the range of the apparatus. Similarly, the very hard materials will give more "reasonable" results if pulled apart very slowly. Convenient speeds are 1, 5 and 25 cms. per minute. Some indication of the value of this technique may be gained from the figures in Table III :—

TABLE III.

Typical Ductilities at Various Speeds.

Bitumen.	25° C.			35° C.			45° C.		
	1 cm. min.	5 cm. min.	25 cm. min.	1 cm. min.	5 cm. min.	25 cm. min.	1 cm. min.	5 cm. min.	25 cm. min.
A	0·5	0·5	Nil	15	8	3	82	59	20
B	2·5	Nil	Nil	115	26	Nil	150	124	145
C	45·6	26·5	11·0	150	75	56	140	145	150
D	5·0	1·5	Nil	28	11·5	5	50·5	38	30

Apart from the modification of existing apparatus, it is necessary to have apparatus specially designed for absolute measurement if a complete picture of the rheological properties of a wide range of materials is to be

obtained. The more important of these may be classified under the following group headings :—

(1) Falling-sphere viscometers.
(2) Rotating-cylinder viscometers.
(3) Coaxial-cylinder viscometers.
(4) Micro and other viscometers.

Falling-Sphere Viscometers.

The principle of viscosity measurement by determination of the rate of fall of a solid sphere through the material under test is probably one of the soundest scientific methods, and is based upon the following equation :—

$$\eta = td^2(\sigma - p)g/18s(1 + 2{\cdot}4d/D)(1 + 5d/3h)$$

where η = viscosity in poises,
g = 981 cm./sec.^{2},
d = diameter of sphere in cm.,
σ = density of sphere (gm. per c.c.),
p = density of liquid (gm. per c.c.),
s = distance between two marks (cm.),
t = time (secs.) for the sphere to fall distance s,
D = diameter of viscometer jar (cm.),
h = height of column of liquid (cm.).

Unfortunately the majority of bitumens are too opaque to permit of visual observation of the fall of a (steel) ball, but the fall may be detected electrically or by an X-ray method evolved by Broome and Thomas [13] and by Barr and Thorogood,[14] respectively.

A useful modification of the falling-sphere method is the inclined apparatus of Höppler.[15] For accurate work with the ordinary falling-sphere viscometer the diameter of the viscometer jar should be not less than ten times the diameter of the falling ball, but the Höppler modification is designed to employ a ball only slightly smaller than the internal diameter of the tube in which it falls. The viscosity is calculated in accordance with the equation :—

$$\eta = F \times (S_k - S_f) \times K$$

where F = time of fall of the sphere through 5 cm.,
S_k = density of the sphere,
S_f = density of the liquid under test,
K = a constant determined experimentally for each apparatus.

These falling-sphere viscometers are, however, only suitable for the measurement of relatively low viscosities, the practical limit having been found to be approximately $1{\cdot}2 \times 10^4$ poises. They can, therefore, only be used for the examination of normal types of asphaltic bitumen at relatively high temperatures, and the author feels strongly that most attention should be paid to the temperatures at which the material will exist in practice on the road, in the building and so on—*i.e.*, over the normal atmospheric temperature range. Attention is therefore directed to the alternative methods.

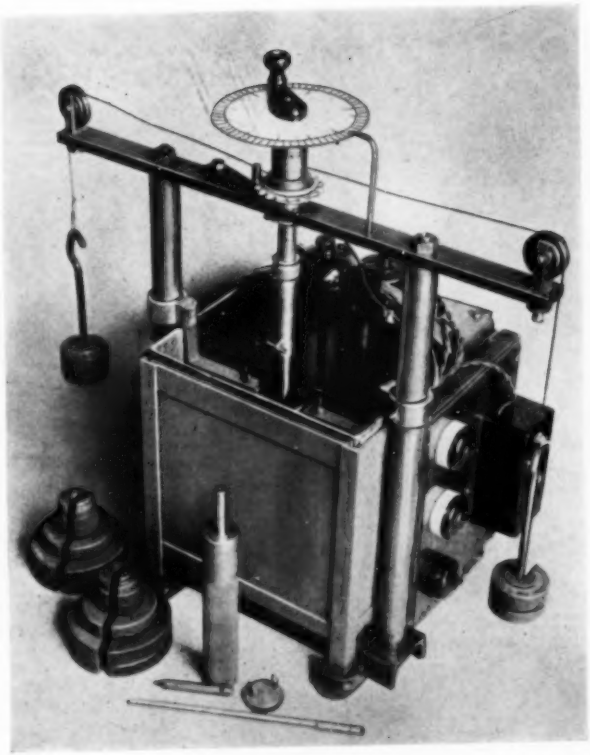


PLATE I.

ROTATING-CYLINDER VISCOMETER.

[*To face p.* 514.

Rotating-Cylinder Viscometer.

There are two possible methods of carrying out viscosity determinations by observation of the relative movement of two cylinders of bitumen, etc., in the intervening annular space, namely :—

(*a*) Measurement of the speed of rotation of an inner cylinder actuated by a known force, the outer cylinder being kept stationary.
(*b*) Measurement of the torque acting on the inner cylinder when the outer cylinder is rotated at a constant angular velocity.

Principle (*a*) was first suggested by Couette,[16] and has since been modified by others, but, in relation to the present problems, particularly by Mooney and Ewart.[17] The general form of the apparatus as used by the author is shown in Plate I, and, as will be seen, the inner cylinder is rotated by means of falling weights, the viscosity being subsequently calculated in accordance with the equation :—

$$\eta = \frac{mgr}{8\pi^2 lw}\left(\frac{1}{r_2^2} - \frac{1}{r_3^2}\right)$$

where m = load in grams,
g = acceleration due to gravity,
r = radius of pulley plus cord (cm.),
r_2 = radius of inner cylinder (cm.),
r_3 = radius of outer cylinder (cm.),
l = length of inner cylinder immersed (cm.),
w = velocity of inner cylinder (revs. per sec.).

The mean shearing stress is given in dynes per sq. cm. by the equation :—

$$F = \frac{mgr}{(r_2 - r_3)^2 l}$$

It will be noted that in these equations there is no correction for any error resulting from " friction " between the bottom of the inner cylinder and the bitumen. This " end correction " has been deleted by the use of mercury in the bottom of the container to an amount just sufficient to cover the lower end of the inner cylinder. The remaining error by this method is much less than the general experimental error, and has been found very satisfactory in practice. Slip at the surface of the inner cylinder is prevented by fine corrugation of this cylinder. The principal advantage of this apparatus is that materials can be sheared for any desired length of time in one direction at constant shearing stress. Also the rotating cylinder viscometer permits measurements over a wider range of consistency than most other types of instruments.

The apparatus in which the outer cylinder is rotated and the torque acting through the bitumen to the inner cylinder being the factor actually measured, may be typified by that used by J. Csagoly.[18] He gives the following equation for this method :—

$$\eta = \frac{K}{cv}$$

where K = the torque acting on the inner cylinder,
c = an apparatus constant,
v = the angular speed of rotation of the outer cylinder.

This is ingenious, and doubtless useful for certain purposes, but for normal bitumen work its viscosity range is too low to permit of atmospheric temperature measurements.

Coaxial Cylinder Viscometers.

Although the rotating-cylinder viscometers just described are in fact coaxial cylinder instruments, this term is usually used only in reference to coaxial cylinder arrangements in which the inner cylinder is moved longitudinally through the outer cylinder without rotation. The use of this principle for study of the rheological properties of bitumens was first demonstrated by Traxler and Schweyer,[19] although originally suggested for other materials by Segol [20] and Pochettino.[21] In the form of apparatus recommended by Traxler,[22] the bitumen under test is poured into the annular space between two cylinders and, after cooling, the whole is supported vertically and a load applied to the inner cylinder so as to displace this through 1 mm. From the time in seconds necessary to effect this displacement, the viscosity may be calculated. The calculations necessary for this have been studied, notably by Tolstoi [23] and by van Nieuwenburg.[24] In most cases the conditions are represented by the equation :—

$$\eta = \frac{Pg}{2\pi Vh} \, e \log \frac{R_2}{R_1}$$

where V = the velocity of the inner cylinder,
P = the weight of the inner cylinder,
h = the length of the inner cylinder in contact with the bitumen,
g = acceleration due to gravity,
R_1 = the radius of the inner cylinder,
R_2 = the radius of the outer cylinder,
η = viscosity in poises.

Traxler's apparatus in its latest form [25] is so constructed that with a given weight the number of seconds required for a 1 mm. movement multiplied by 100,000 gives the viscosity. In this way a determination of viscosity can be made in this apparatus in less time than is required for a penetration test, and it has been found very suitable for a study of age-hardening over short periods of time under conditions where no differences are shown by the penetrometer.

Other Viscometers.

Although the scope of this paper precludes a detailed study of all the viscometers suitable for the study of the flow properties of bitumen, the following additional methods may be referred to, details being available in the original literature :—

(1) A modified capillary-tube viscometer for 10–1,000,000 poises.[26]
(2) The alternating-stress method suggested by Bingham and

Stevens [27] and developed with particular regard to bitumens by Traxler and others.[26, 28, 29] This is suitable for 10^5–10^8 poises.

(3) A rod viscometer, suitable for about 10^7–10^{13} poises.[30]

(4) Sinker viscometer, used by several workers, notably by Saal.[31] Suitable for 0·1–10^5 poises.

(5) Disc viscometer, proposed by Obermayer [32] and developed by Manning [33] suitable for 10^7–10^{12} poises.

In addition to the above, reference might be made to the following instruments, particularly suitable for the examination of bitumen, etc., at viscosities of less than about 100 poises.

(1) The torsion viscometer as used by Fuidge,[34] and advocated by the Standardization of Tar Products Tests Committee.[35, 36]

(2) The trough viscometer.

(3) The metro plastimeter, both developed by Evans and Pickard.[37]

(4) The ball-and-bucket viscometer of Beale and Docksey.[38]

(5) The British road-tar viscometer.[39]

(6) The modified Ostwald viscometer proposed by Lee.[40]

If the quantity of material available for test is very small, the methods of Levin [41] and of Bondi [42] may frequently be employed.

Plasticity.

It has already been noted that the majority of bitumens are not true fluids at normal atmospheric temperatures, and this deviation has been studied particularly by means of the Couette type viscometer. It was originally suggested by Bingham [43] that, whereas true fluids give straight-line curves passing through the origin if rate of shear is plotted against shearing stress, other materials give curves such as *B* in Fig. 2, in which for shearing stress below a certain value no appreciable shearing motion appears. Bingham's idea is to extrapolate the experimental curve to the stress axis, and to take two constants, the intercept and the slope. The intercept was originally called "yield-value" or "critical shearing stress," but is better named "shearing strength." The slope has been called "pseudo-viscosity" or "stiffness." It was at one time erroneously called "plasticity." Its reciprocal is "mobility" or "liquidity." Saal [30] pointed out that bitumens can give curves of an intermediate type such as *C* in Fig. 2, where the ratio shear/stress increases with rate of shear up to a relatively high stress. This does, in fact, seem to represent the behaviour of many asphaltic bitumens, although under certain conditions curves of type *D* have been obtained with shear/stress ratios *decreasing* with rise of shearing stress over the lower part of the curve. This phenomenon remains largely unexplained, but it is interesting to note that it is particularly apparent in the case of highly elastic materials such as rubber–bitumen mixtures.

The identification of the presence of a "yield value" or "shearing strength" is difficult, and apparently depends largely on test conditions, it being very doubtful whether any of the asphaltic bitumens normally employed in this country have definite yield points. Study at low rates of shear (less than 0·01 cm. per sec.) has, however, given some indication of the "apparent shearing strength," although the methods of examination are

not as accurate as might be desired at rates of shear lower than about 5×10^{-3} cm. per sec. Some typical curves are shown in Fig. 3, which would indicate shearing strengths of the order shown in Table IV :—

TABLE IV.

Typical Shearing Strength Figures at 30° C.

Bitumen A	$0{\cdot}7 \times 10^3$
Bitumen B	1·2
Bitumen C	5·2

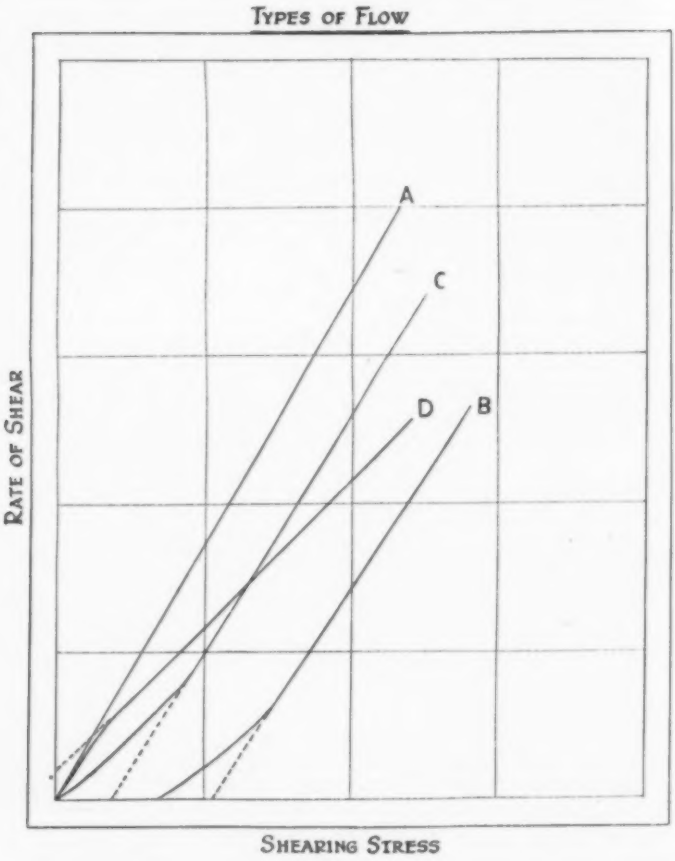


FIG. 2.

An interesting treatment of results obtained with viscometers such as the rotating concentric cylinder instrument consists in plotting log rate of shear

against log shearing stress. This gives approximately straight lines, which may be represented by the equation :—

$$v = kF^p$$

wheer v = rate of shear,
k = a constant,
F = shearing stress,
p = the slope of the curve.

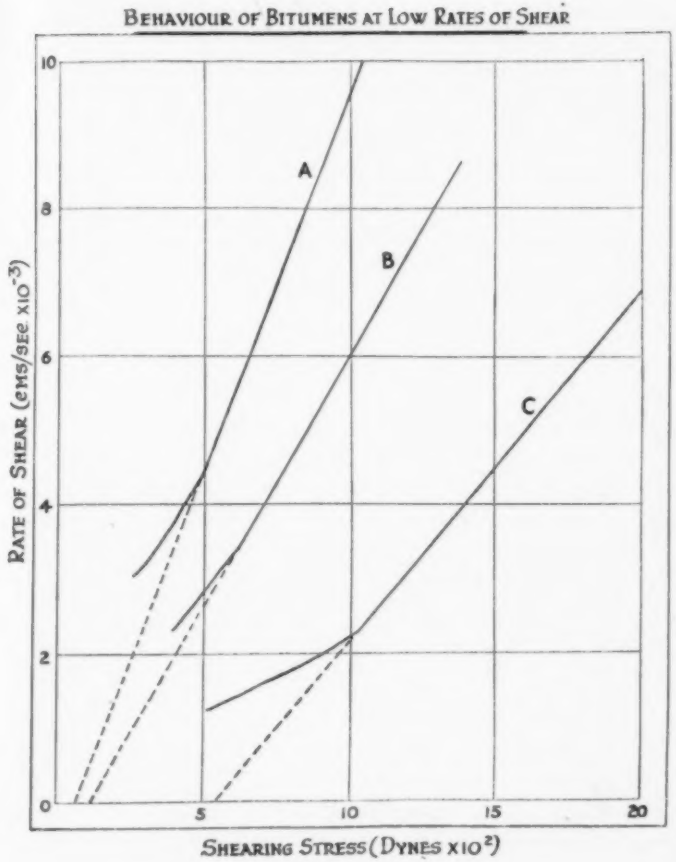


FIG. 3.

The value of p may also be regarded as a measure of the plasticity of the material, the higher the value the greater being the deviation from being a true fluid. Some typical values of p are given in Table V.

TABLE V.

	Value of p.	
	25° C.	60° C.
65 Pen. Bitumen A . .	1·07	1·03
200 Pen. Bitumen A . .	1·04	1·0
200 Pen. Bitumen B . .	1·42	1·21
200 Pen. Bitumen C . .	1·78	1·33

It has been found that, as illustrated by the figures in Table V, the value of p generally tends to fall somewhat with rise of temperature, although some anomalies have been noted with regard to this, presumably owing to thixotropic and work-hardening complications. Moreover, comparison with Table II shows that this method is considerably less sensitive a measure of plasticity than that referred to in the early part of this paper.

THIXOTROPY.

The presence of thixotropy is readily apparent when bitumens are examined by the methods already described, the speed of rotation of the inner cylinder frequently increasing appreciably as the test proceeds. Occasionally, however, a kind of "inverted thixotropy" is observed, which has been described as "work hardening" or a "winding spring effect." This has been found particularly in the case of materials that are highly elastic, such as rubber–bitumen mixtures. This is illustrated in Fig. 4. It has been suggested that this is due to the molecular arrangement becoming more regular under the strain. This greater regularity is, thermodynamically, less probable, and the material therefore develops a stress in an attempt to revert to a less ordered or thermodynamically more probable state.

AGE-HARDENING.

In the examination of thixotropic phenomena it is very necessary to have a full knowledge of the thermal history of the sample under test.

Care is always taken in the laboratory to ensure that the temperature throughout the sample is adjusted to the test temperature, but this is not sufficient when studying rheological problems of bitumens. Even standing overnight is sufficient to show this phenomenon, as may be illustrated by the curves of Fig. 5. Tests *repeated* on this same sample frequently show evidence of age-hardening and thixotropy (Fig. 6).

ELASTIC RECOVERY.

Data concerning elastic recovery may be obtained with the concentric cylinder viscometer in the same way as with the twisting-sample method—*i.e.*, by permitting rotation through a convenient angle, and then removing the shearing stress and measuring the angular recovery after the material has come to rest. The figures recorded must only be compared with other elasticity data with caution, as they are found to vary according to :—

(*a*) The rate of shear prior to release of the load.
(*b*) The angle through which the sample has been displaced.
(*c*) The dimensions of the test specimen.
(*d*) The temperature of test.

Care must also be taken to ensure that ample time is allowed for the sample to come to rest. This takes very much longer than is sometimes

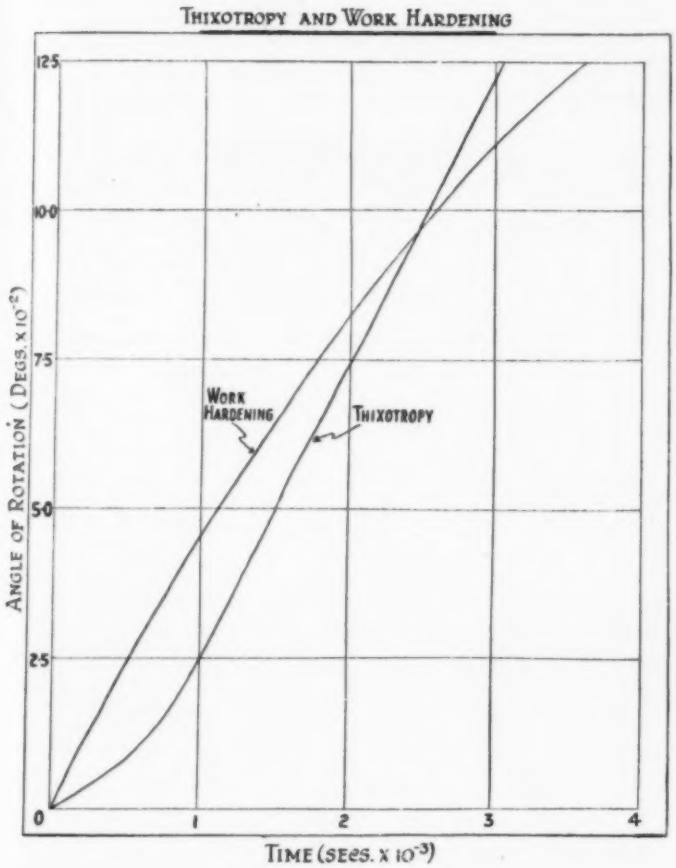


FIG. 4.

realized, and may be illustrated by Fig. 7. A few typical recovery figures are given in Table VI.

TABLE VI.

Bitumen.	Penetration at 25° C.	Temperature.	Elastic Recovery.
Steam Refined Bitumen . . .	200	0° C.	30°
Steam Refined Bitumen . . .	200	15° C.	10°
Do. plus 1% Rubber . .	150	0° C.	62°
Do. plus 1% Rubber . .	150	15° C.	40°
Fluxed Lake Asphalt . . .	203	0° C.	37°
Fluxed Lake Asphalt . . .	203	15° C.	15°
Do. plus 1% Rubber . .	170	0° C.	67°
Do. plus 1% Rubber . .	170	15° C.	35°
200 Pen. Asphaltic Bitumen 80% / Trinidad Lake Asphalt . 20%	—	0° C.	60°
Oxidized Bitumen	40	15° C.	130°

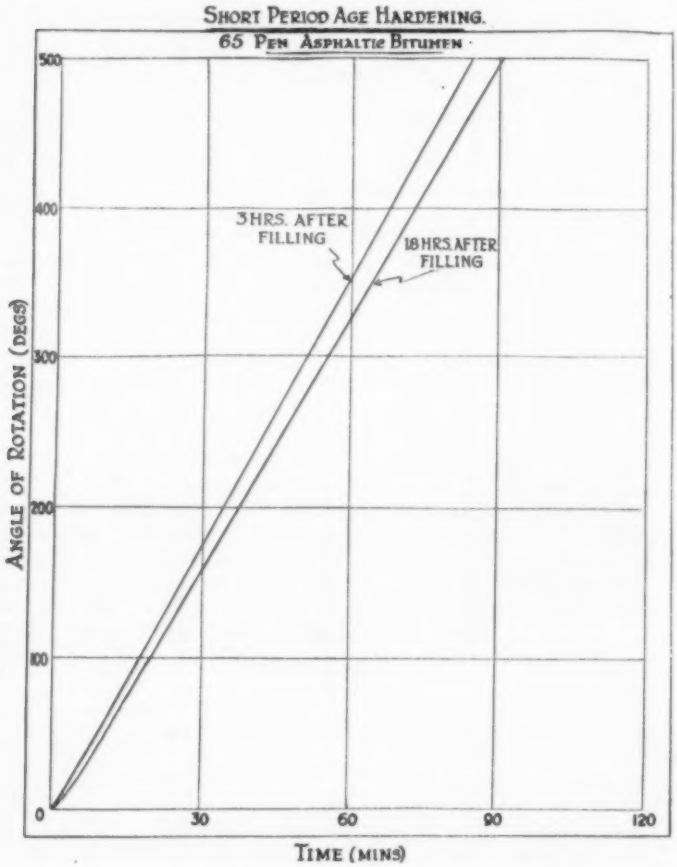


FIG. 5.

Viscosity–Temperature Relationship.

It is obviously of very considerable importance to have a knowledge of the "temperature susceptibility" of any bitumen to be used for such work as the manufacture of asphalt for road or building construction, and it may be of value to review briefly some of the methods that have been proposed for this purpose.

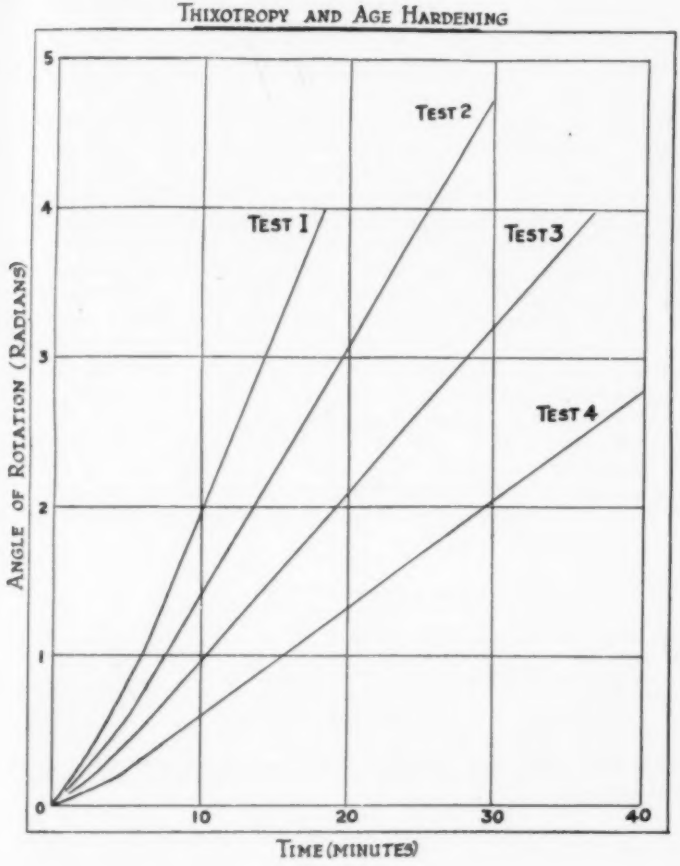


Fig. 6.

An early method consisted merely in recording the extent of the plastic range—*i.e.*, the temperature difference between the softening point (*e.g.*, by Ring and Ball) and the brittle point (*e.g.*, by Fraass). Later methods suggested graphical methods based on rather complex equations. For example, Saal [44] obtains a straight line relationship by plotting :

$$\log \log (V_t + 1) = m \log T + c$$

where V_k = kinematic viscosity (centistokes),
T = absolute temperature,
$m + c$ = constants.

Umstatter [45] suggests plotting log viscosity against the reciprocal of the square of the absolute temperature, thus :—

$$\log \eta = mT^{-2} + C$$

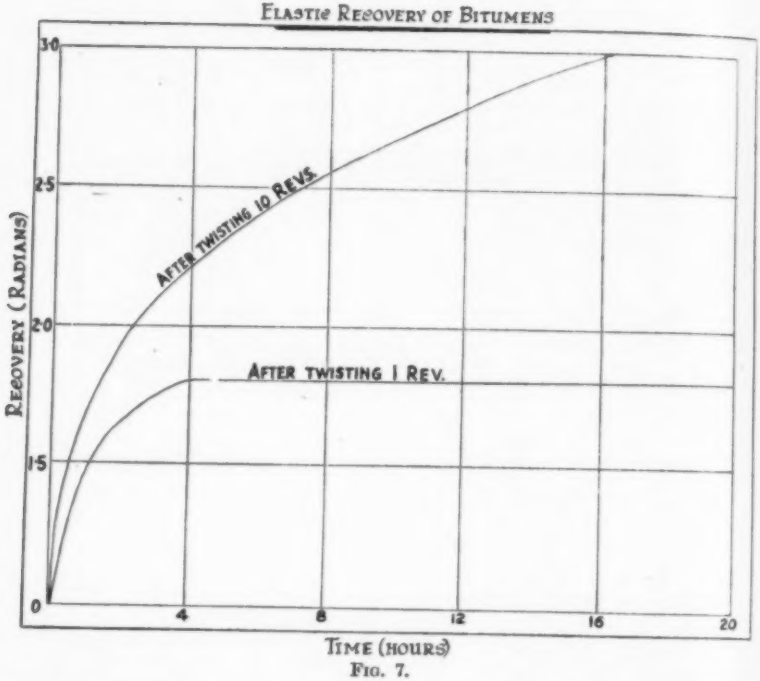


FIG. 7.

The A.S.T.M.[46] have proposed two susceptibility factors based on penetration tests :—

$$\text{Susceptibility} = \frac{\text{Pen. } 115^\circ \text{ F., } 50 \text{ g., } 5 \text{ sec.} - \text{Pen. } 32^\circ \text{ F., } 200 \text{ g., } 60 \text{ sec.}}{\text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.}}$$

$$\text{Susceptibility} = \frac{\text{Pen. } 100^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.}}{\text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.}}$$

Both these are unsound, as in the former the consistency is measured at three different and unknown stresses, and in the latter again in unknown stresses which change at different rates.

A fluidity factor has been proposed by Zapata [47] :—

$$\text{Fluidity} = \frac{(\text{Furol Vis. } 275^\circ \text{ F.} - \text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.})}{(\text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.})/100}.$$

Somewhat similar is Kelley's float-test index [48] :—

$$\text{Float-test Index} = (\text{Float } 176^\circ \text{ F.} \times \text{Pen. } 77^\circ \text{ F., } 100 \text{ g., } 5 \text{ sec.})^{\frac{1}{2}}$$

Also Abraham's susceptibility factor [49] :—

$$\text{Susceptibility} = \frac{\text{Hardness at } 32^\circ \text{ F.} - \text{Hardness at } 115^\circ \text{ F.}}{\text{Softening Point (K. \& S.)}} \times 100$$

All these suffer from the disadvantage of trying to reconcile figures obtained at different, varying, and frequently unknown, stresses. They are arbitrary formulæ with no scientific basis.

Pfeiffer and van Doormal [50] proposed a scheme for a " penetration index " which must be criticized somewhat in the same direction, as it is obtained by means of a nomogram establishing a relationship between the penetration and the Ring and Ball softening point. The scheme is particularly doubtful, as it assumes that the Ring and Ball point corresponds to a penetration of 800, whereas actually the softening point may correspond to penetrations ranging from about 450 to 1000 or more. This wide variation of consistency at the Ring and Ball point seems generally not to be realized, possibly because it is not possible to measure penetration at that temperature. With the aid of the Couette type viscometer, however, viscosities may readily be determined at the softening point. If this is done, it will be found that not only do bitumens have widely divergent viscosities at this temperature, but that the viscosity is still generally dependent on the stress applied. A few typical figures are shown in Table VII :—

TABLE VII.

Viscosity at the Softening Point.

Bitumens.	R. & B. Softening Point, ° C.	Viscosity at R. & B. Point.
Venezuelan Mexphalte 65° . .	52	$2{\cdot}4 \times 10^4$ poises.
Ditto plus 2% Rubber . . .	65	2·3
Venezuelan Mexphalte 200° . .	40	1·6
Ditto plus 2% Rubber . . .	47	2·1
Trinidad A.C. (200 Pen.) . . .	40·5	2·2
Ditto plus 2% Rubber . . .	65·5	1·9

A sounder temperature susceptibility scheme is that employed by Mitchell and Lee [51] :—

$$n = (\log \eta - \log \eta_2)/\log T_2^\circ \text{ F.} - \log T_1^\circ \text{ F.}$$

where n = the logarithmic temperature coefficient

η_1 = viscosity at T_1° F.

η_2 = viscosity at T_2° F.

This scheme gives figures such as those in Table VIII when applied to data obtained with the Couette type viscometer :—

TABLE VIII.

Logarithmic Temperature Coefficients.

Venezuelan Mexphalte 65°	9·4
Ditto plus 2% Rubber	10·8
Venezuelan Mexphalte 200°	8·2
Ditto plus 2% Rubber	8·3
Trinidad A.C. (200 Pen.)	10·2
Ditto plus 2% Rubber	10·0

It must, however, be pointed out that log viscosity/log temperature curves, although straight lines in many cases, are rarely parallel lines and, not only does the rate of change of viscosity with respect to temperature vary with temperature, but the slope of the curve is also dependent on the shearing stress employed. A better way of expressing temperature susceptibility is to measure the percentage decrease in viscosity (in absolute units) for 1° C. rise in temperature over the suitable temperature range. The method was proposed by Traxler and Schweyer,[52] who express the numerical value of the susceptibility by the equation :—

$$\text{Asphalt Viscosity Index (A.V.I.)} = 100\,[(\eta_c/\eta_d)^{1/(t_c - t_d)} - 1]$$

where η_c and η_d are the viscosities, in poises, of the bitumen at temperatures t_c and t_d (°C.). The values for the A.V.I. are negative, since the viscosity decreases with temperature, but the sign may be neglected without detracting from the value of the index. A few typical figures are given in Table IX :—

TABLE IX.

Asphalt Viscosity Index.

200 Pen. Venezuelan Mexphalte	19·3
Ditto plus 2% Rubber	18·3
200 Pen. Trinidad A.C.	21·5
Ditto plus 2% Rubber	20·0

With either of these methods care should be taken to employ them only over a relatively small temperature range as the variation of viscosity with temperature is very complex, probably owing to the complex structure of bitumen. It would appear probable that the structure changes very considerably as the material is heated or cooled, so that with rise of temperature a bitumen may be regarded as passing successively through the following states :—

Solid—" plastic solid "—" liquid plastic "—liquid.

The first of these changes corresponds very approximately to the brittle point, whilst the last of these changes is a gradual process taking place above the " melting point." For any given bitumen the change from one state to another will take place at different temperatures, depending on the rate of change of temperature, etc., and will certainly take place at different temperatures, according to whether the material is being heated or cooled. The situation is further complicated by the phenomena of thixotropy and work-hardening, the condition at any moment being a matter of equilibrium between the process of transformation in the direction solid–liquid and the transformation in the direction liquid–solid. Further, the test operation

normally upsets the equilibrium, so that the test results obtained may vary within wide limits, according to the conditions.

The author wishes to record his thanks to Mr. T. A. Sharpley, who has given considerable assistance with the experimental work.

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Fulham, S.W.6.

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DISCUSSION.

Mr. L. J. Chalk wrote: Mr. Broome has given us an extremely interesting survey of the flow properties of bitumens, and has raised a number of points of considerable practical and theoretical importance. One of these concerns methods of obtaining a numerical index for what is generally referred to as "plasticity." The normal laws of viscous flow do not apply to most bitumens, and, as a consequence, the figure obtained for viscosity varies with the shearing stress; whence it follows that the function referred to as "degree of plasticity" is not a true constant. In the case of the twisting-cylinder apparatus, the observed viscosity, and therefore the "degree of plasticity," will depend on the weight used to apply the torque, the dimensions of the test specimen, and diameter of torque drum. The "degree of plasticity" cannot therefore be accurately interpreted or the figures reproduced by other laboratories, unless the precise conditions under which the test was carried out are known. A further point is that the figures given in Table I convey rather a false impression of the accuracy of the results obtained by the twisting-cylinder method. It is rarely permissible, even with true fluids, to express viscosity to more than three significant figures, and I think Mr. Broome will agree that this would have been ample in the present instance.

An alternative method of expressing plasticity is based on the fact that the equation $V = KF^P$ has been shown to hold for a number of bitumens. The equation does not itself represent a straight line (as stated on p. 519), but on taking logarithms it reduces to the form $\log. V = \log. K + p \log. F$, which experimentally is found to be a straight line. The amount by which "p" is greater than 1 is the measure of the plasticity of the bitumen. The term "p" is a true constant, and, for this reason, would appear to be more suitable as an index of plasticity than the function "degree of plasticity."

Dr. F. H. Garner wrote: The paper by Mr. Broome represents a valuable summary of all the various properties comprised under the term "flow properties of bitumen," and it is interesting to have a description of the two types of apparatus which he has used for the measurement of these properties—namely, the Frankland–Taylor twisting-point apparatus and the modified rotating-cylinder viscometer.

It would appear that the plasticity figures quoted in Table II are of limited value, since it is doubtful whether it is possible to derive the degree of plasticity from a relationship between the observed viscosity at 25° C. and a figure for viscosity calculated from the penetration; this is based on the assumption that true viscosity is dependent only on penetration, but there are other factors concerned in penetration. On the other hand, Dr. Lee stated that in the case of practically all bitumens the curve obtained when the shearing test was plotted against rate of flow was a curve passing through the origin, and hence plasticity can be measured by the P in the formula:—

$$V = kF^P.$$

This would appear to be a much sounder measure of plasticity, but here again the plasticity may vary with the rate at which the shearing stress is applied, as illustrated by the figures quoted in Mr. Broome's paper.

Mr. R. Preston wrote: Mr. Broome has performed useful work in indicating the large number of methods adopted or suggested for determining the flow properties of bitumen, and although there appears to be little exact knowledge published on the correlation between laboratory tests and practice, he has directed attention to this problem by his statement of preference for the more plastic bitumens for road work, and for those of maximum ductility.

I would venture a few observations on these two properties. Mr. Broome was perhaps among the first to adopt a method of expressing plasticity in terms of a simple control test (penetration), but the very wide range of values for the "degree of plasticity" of different bitumens obtained by his method casts doubt either on the accuracy of correlation with practice, or on the method of deriving the "plasticity." The differences given in Table II of the paper for normal bitumens (as distinct from asphalts) are far too great to be truly significant of their behaviour in practice. A more reliable indication of plasticity which could be determined almost as easily as

that given by Mr. Broome could be obtained by the measurement of flow under a series of different loads. The deformation of a plastic material may be written :—

$$D = F(t)f(S)\phi(\theta)$$

where t = time,
S = stress,
θ = temperature.

Under constant time and temperature

$$D = Kf(S)$$

an equation similar to that given by Mr. Broome on p. 519. Variations in D may be related to variations in S. For example, the relation between penetration and load would provide an index of plasticity, but a test on the lines of the Pochettino viscometer would be preferable, the relation between deformation and load being determined under fixed conditions of time and temperature.

It is open to question, however, whether the quality of bitumens in relation to roads can be assessed independently of their behaviour in presence of mineral matter, and without considering the nature of traffic forces. The writer found some years ago that the deformation of a beam containing mineral matter and a " viscous " binder allowed to sag between pivots could be divided into two stages—namely, a comparatively rapid movement in the initial stage, followed by a longer and steadier movement. On removal of the load, a definite recovery effect was noticed. The initial rapid rate of sag and final " recovery " were obviously manifestations of storage and release of energy. In view of the impulsive nature of traffic forces, it would appear that the phenomena mentioned more nearly represent actual road conditions than the flow under steady load conditions (plastic or viscous flow) except perhaps in the case of heavy slow traffic.

Mr. Broome has given examples of the effect of temperature on ductility, and has deduced that the superiority in practice of bitumen B over C is due to its higher maximum ductility when tested over a range of temperatures. The writer would suggest another explanation for this superiority—namely, its greater ductility at lower temperatures. It would be of interest in this connection to know the values of bitumen A of Fig. 1 compared with bitumens B and C.

Dr. R. N. J. Saal wrote : In Fig. 2, line D is given as a special type of plasticity curve which—according to Broome—is particularly found in the case of highly elastic materials such as rubber–bitumen mixtures. It seems to us that it is the elastic properties of the materials which are responsible for the phenomenon referred to. For, high elastic deformability involves, in the case of a deformation under constant shearing stress, that at the beginning of the determination the rate of shear strongly decreases with time, and subsequently becomes constant or increases again owing to thixotropy.

Hence it will entirely depend on the moment at which the determination is carried out, what value is found for the rate of shear. In the case of the measurements plotted in Fig. 3, " Behaviours of Bitumens at Low Rates of Shear," the interval between the beginning of the deformation and the measurement was perhaps too short to reach a state of elastic deformation corresponding to that in the determinations at higher rates of shear.

One is inclined to seek the explanation of the phenomenon referred to particularly in the circumstances under which the measurement was carried out, because neither line D of Fig. 2 nor the curves of Fig. 3 should ever intersect the rate of shear axis at positive values.

A similar reasoning may be set up for determinations carried out at constant rate of shear.

Furthermore, we would comment on the last chapter, in which the Penetration Index according to Pfeiffer and van Doormaal is criticized. This penetration index is based on the, experimentally found, linear relation between log. penetration and temperature; the slope of the log. penetration–temperature curve indicates the temperature susceptibility. However, since the determination of the temperature susceptibility from two penetrations offers considerable practical drawbacks when applied to bitumens of widely divergent properties, Pfeiffer and van Doormaal preferred

deriving the required slope from one penetration and the softening point R. & B. This is feasible only if the softening point R. & B. invariably corresponds to about the same penetration.

From penetration measurements at softening point R. & B. with a wide range of bitumens it appeared that the penetration at this point is indeed about 800. In some cases deviating values were found (max. 900, min. 600). The influence of these deviations on the calculated temperature susceptibility is, however, comparatively small, as we are here dealing with the log of the penetration, so that the errors in the calculated temperature susceptibility are of but minor importance in practice. The errors involved in the use of two penetrations are, partly on account of the log. penetration–temperature line not being completely straight, of the same order of magnitude.

We would further point out that the differences found for the square of the penetration at softening point R. & B. are of about the same order of magnitude as the differences in viscosity at this point.

Broome prefers to determine temperature susceptibility by measuring the percentage decrease in viscosity (in absolute units) for 1° C. rise in temperature, yet he emphasizes that with this and other methods care should be taken to employ them only over a relatively small temperature range, as the variation of viscosity with temperature is very complex. In our opinion it is the chief advantage of the system proposed by Pfeiffer and van Doormaal that the relation between log. penetration and temperature is not complex, but practically linear over a rather wide temperature range. This even applies in the case of blown bitumens, where, on account of elasticity and thixotropy, it is not possible to characterize the behaviour by means of a single absolute viscosity determination.

Mr. D. C. Broome in reply wrote that he fully appreciated that the degree of plasticity as determined by means of the twisting-cylinder apparatus depended on the weight used to apply the torque, the dimensions of the test specimen, and the diameter of the torque drum. This meant that the test was an arbitrary one, and possibly the equation suggested by Mr. Chalk was theoretically sounder. From a practical point of view, however, he had found that the former method was extremely useful, and did seem to magnify the differences in plasticity between various materials in a manner which lined up with practical experience.

He agreed that the data in the last column in Table I should only have been quoted to three significant figures.

He also agreed that the alternative method of expressing plasticity to which Mr. Preston referred was, of course, quite reliable, but he had found, as a result of experience, that the method referred to in the paper was extremely useful in virtue of the very fact that it did magnify the differences. The situation there was somewhat analogous to the use of a microscope for examining small particles. One did not see the true size of the particles when examined under the microscope, but their very magnification was extremely useful in assisting their evaluation.

He fully agreed that the properties of the bitumen in a road were affected very materially by the presence of mineral matter. His experience was, however, that plastic or viscous flow did frequently take place under practical road conditions, and that was therefore a contributory factor, although it was certainly not the only factor.

With regard to the ductility of bitumens *B* and *C* in Fig. 1, his view was that bitumen *B* was superior not merely because it had a higher maximum ductility, but also because that maximum ductility occurred at an appreciably higher temperature. It was also superior in that its ductility at very low temperatures was greater.

BITUMEN EMULSIONS—THEIR DEVELOPMENT AND PRESENT SPHERE OF UTILITY.*

By L. G. Gabriel, B.Sc., A.I.C., F.Inst.Pet.

Summary.

The historical development of the manufacture of bituminous emulsions is sketched and various problems which had to be solved in order to remedy the initial difficulties are dealt with. Data are given of the types of emulsion obtained with various pure chemical compounds. Sedimentation behaviour of emulsions is considered and experimental results are quoted, showing the evaporation behaviour of emulsions. Problems underlying the chemical interaction of bituminous emulsions and stone aggregates are dealt with and the specific nature of these chemical reactions, as between any given emulsion and any given stone aggregate, is demonstrated. The physico-chemical factors underlying the viscosity/concentration relationships of bituminous emulsions are discussed in detail and the general formula of Hatschek is shown to apply. Methods of use of emulsions on the road and in industry are described and the mechanism of the breakdown of these emulsions in various circumstances is analysed. The special types of emulsion, developed for industrial purposes, are briefly considered and the development of the industry as a whole, from its beginnings to its present scientifically controlled achievement, is summarised.

The purpose of the present paper is to present, more particularly for the non-expert reader, an account of the development of the manufacture and use of bituminous emulsions of all types, and the rôle they now fill. In the course of the survey it is proposed to deal with development in manufacture and in application, and also to indicate one or two typical examples of the growth of technical knowledge in this territory, as the result of intensive research which has been carried out in the industry. It will be seen that this research work, in some cases, has applications which come outside the immediate sphere of use of bituminous emulsions, and has more general significance.

The underlying idea of the endeavour to emulsify bitumens is, of course, a cheap method of rendering them more fluid and, therefore, easier to apply. The use of bitumen, heated to render it fluid, antedated its use in the emulsion form or as cutback, but the disadvantages which were felt led to a search for a more convenient type of material, still possessing the binding and waterproofing power of bitumen. These drawbacks were principally, of course, the inconvenience, in certain circumstances, of having to heat the bitumen and, further, the care which has to be exercised if real control is to be obtained over the rate and conditions of application, in view of the rapid increase in viscosity which takes place as the heated binder cools to air temperature. It seems probable that the use of bitumen emulsion—that is, bitumen fluidified with water as the medium—antedated, at any rate on the large scale, the use of bitumen fluidified with solvent (cutbacks), merely because the cheapness of water appealed to the imagination of early workers. At any rate, we can go back to the year 1904 for the first appearance of a patented process for the emulsification of bitumen. Actually, this had been preceded in 1903 by a patent taken out by van Westrum for

* Paper presented to a Meeting of the Asphaltic Bitumen Group of the Institute of Petroleum held on 9th May, 1939.

the emulsification of dust-laying oils. Quite a dozen other specifications for emulsifying bitumen appeared before 1910, in which year van Westrum's well-known patent for a process of this kind was taken out.

A certain amount of application of this and similar patents occurred immediately prior to the Great War, but development on a large scale was not forthcoming, and one of the reasons for this was that bitumens, in those days, were probably not as amenable to emulsification as they were after the great improvements in refinery technique which took place immediately after the War, and, further, the quantities of emulsifying agent specified in the early processes were, in our view nowadays, excessive, although here again this may have been conditioned by the characteristics of the then available bitumens. The emulsions, in any case, once made, undoubtedly possessed, for the most part, properties similar to those which we now class as semi-stable, and, as such, it is not altogether surprising that difficulties to do with setting seemed to have resulted in a discouragement of early efforts.

After the War, however, the problem of the reconstruction and modernizing of the road system of European countries began to come to the fore, with the greatly increased development of motor traffic. A large mileage of roads in those days consisted of water-bound macadam and, under the greater demands of higher-speed motor traffic, these roads began to show signs of breaking up, and maintenance became a severe problem. It was soon found that in laying the dust by means of emulsified oils and bitumens, a film of the tar or bitumen tended to remain on the road, especially after repeated treatments, and the idea then suggested itself that this film had advantages of its own, and from that time the practice began to emerge of applying heavier dressings than those strictly necessary for dust-laying, and it was only a matter of a short time before the advantages of the bitumen-surfaced road became fully apparent, particularly for pneumatic-tyred traffic.

Manufacture.

The earliest process for the manufacture of bituminous emulsion which had a successful large-scale development was that which appeared in 1922 under British Patent No. 202,021 by Mackay. The emulsion made by this process was responsible for the bulk of the pioneering development of the bituminous road emulsion industry. The process consisted in stirring into the molten bitumen a quantity of fatty acid or other suitable acidic constituent of the ultimate emulsifier, then running in a solution of alkali to saponify this fatty acid in the mixer and in the body of the bitumen to be emulsified, and diluting the rather concentrated emulsion so formed with a sufficient quantity of water. This process gave very satisfactory results with Mexican bitumen, in use at that time, and, provided no unexpected changes in the characteristics of the bitumen supervened, an emulsion of uniform and standard quality was obtained. It must be realized that in those days all who were endeavouring to work emulsification on the large scale, as a scientific process, were handicapped by almost complete ignorance of the fundamental principles involved, and by a very incomplete understanding of the properties of the finished emulsion. The whole thing was rather a miracle. All failures and inconveniences had to be accounted for

by rule of thumb and without very much real understanding. However, standardized methods for the application of emulsion of this type gradually developed, and before many years had elapsed it became evident that the idea was capable of a very considerable future.

At this time various competitive processes began to appear, and, in particular, note should be taken of a series of such processes, all based on the same fundamental idea, which was first set out in British Patent No. 226,032, by Montgomerie, published in 1924. This patent covered a process in which advantage was taken of the fact that bitumen itself contains a small percentage of substances of an acidic nature, which, in combination with alkali, were capable of forming soap-like bodies, which produced emulsification of the bitumen, under conditions of adequate agitation.

In the Montgomerie process a dilute solution of caustic alkali was first placed in the mixer, and into this was allowed to flow the molten bitumen. An emulsion of greater or less stability was formed, according to the precise characteristics of the bitumen, and this was usually further stabilized by the addition, at the end of the process, of a quantity of soap or similar colloidal protective body. The Montgomerie process showed up at once in a favourable light, in view of the fact that the total concentration of soap and alkali present could be established at a figure very much below that required in the Mackay process. Furthermore, the two processes could be carried out in the same type of slow-stirring mixer, in which the blades did not need to revolve at a greater speed than 60–90 r.p.m. Nevertheless, it was found at the time that the properties of the Mackay emulsions were, in some ways, superior to those of many of the emulsions made by the Montgomerie process, and, in any case, in those days competition was not so severe, consequently the prime cost of the ingredients was not so important a factor as it is now.

It will be noted that the Mackay type of emulsion depended less on the chemical composition of any substances present in the bitumen and, in the author's experience, this, on many occasions, proved a boon, in that the Mackay emulsions were less susceptible to any changes in the bitumen than those produced by the Montgomerie process.

It should be explained that these changes in the bitumen were not such as could be detected by determination of the normal physical properties of the bitumen, and at that time the variations were not at all understood, although they are more comprehensible to-day, as will be seen later.

It is curious to note that in those early days methods of control of the viscosity of emulsions were discovered: that is to say, methods by which the viscosity of the emulsion could be raised or reduced, without altering the bitumen content. In the Mackay process the rate of addition of the alkali solution accomplished this, and a certain amount of control, in a similar way, was possible in the Montgomerie process by changing the rate of addition of the bitumen. With Mexican bitumen the changes in viscosity which could be achieved in this way, at any rate with the Mackay process, were quite considerable, and it was possible, given favourable circumstances, to prepare emulsions containing, say, 50 per cent. of bitumen, which had a consistency of thick cream. The explanation of these phenomena, in the light of developments which will be described later in the paper, affords rather an interesting sphere of speculation.

The development and use of these emulsions proceeded smoothly for a year or so, until, in or about the year 1927, a series of quite unusual difficulties in manufacture occurred, at any rate in the author's experience, which necessitated much more fundamental efforts to secure a remedy than had previously been the case. After some little investigation, it became clear that the type of bitumen had changed radically. It must be remembered that at that time such a change over was not thought to have any special significance, and a good deal of surprise was experienced by everyone that the process which had gone smoothly before now showed considerable hesitation and, furthermore, the emulsions, once obtained, were very much less viscous than those obtained previously.

The ultimate result of this setback was that other methods of emulsification came into consideration. There was a prejudice at that time against the use of the newly introduced colloid mill for the dispersion of bitumen, because it was thought it yielded emulsion of tremendous stability. Here again, though ideas on the possible causes of changes of stability were quite rudimentary, there was a general inclination to associate stability with the dispersion, and it was thought that the dispersion produced by colloid mills would be much finer than that produced in the mixer. Trial, of course, readily showed that neither the dispersion nor the stability exhibited these great differences, and it soon became apparent that there was one great advantage in the use of the colloid mill: this was that it rendered the process almost independent of the percentages of acids, resins, and other bodies, which were capable of influencing the emulsification by any process involving saponification in the presence of the bitumen.

The colloid mill, therefore, became increasingly popular for the preparation of bitumen emulsions from that date onwards, although the mixer processes, in more highly developed form, are still finding considerable use.

The use of the colloid mill imposes a very much higher power consumption to produce emulsions; but, nevertheless, this is not a decisive factor, because in any case the power cost is a very small fraction of the total cost of manufacture. As against this it is possible to arrange the mill so that it can be fed by means of a system of grouped pumps for the ingredients which go to the preparation of the final emulsion, and the process is therefore a continuous one, under very good control as regards the proportion of the ingredients.

The type of mill used may vary between almost any of those on the market, but those which have achieved most use in the industry are the Hurrell, the Premier, and the Hatt-Dussek. Figs. 1, 2 and 3, show these three types of mill.

In actual practice they all function on the same principle, which is the subjection of the bitumen and emulsifier solution to very high forces developed in spaces of small dimensions. This has the effect of splitting up the bitumen into small globules, in the presence of the emulsifier solution, which stabilizes them in that form and prevents them again coalescing to the bulk phase. It would be possible to go into great detail on the relative advantages of the different types of mill, but it is not proposed to do this in a general paper of this type. However, one observation should at any rate be made. From time to time the different types of mill on the market are advertised as possessing advantages, due to saving in power consumption,

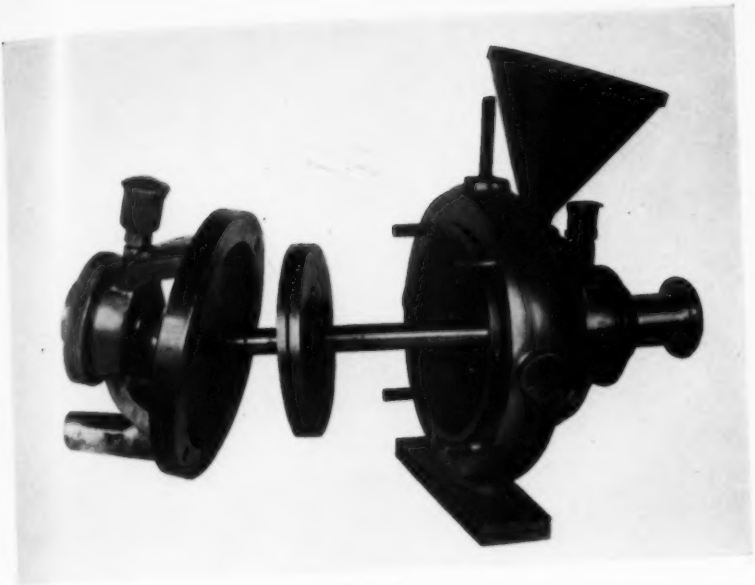

FIG. 1.
HURRELL MILL.

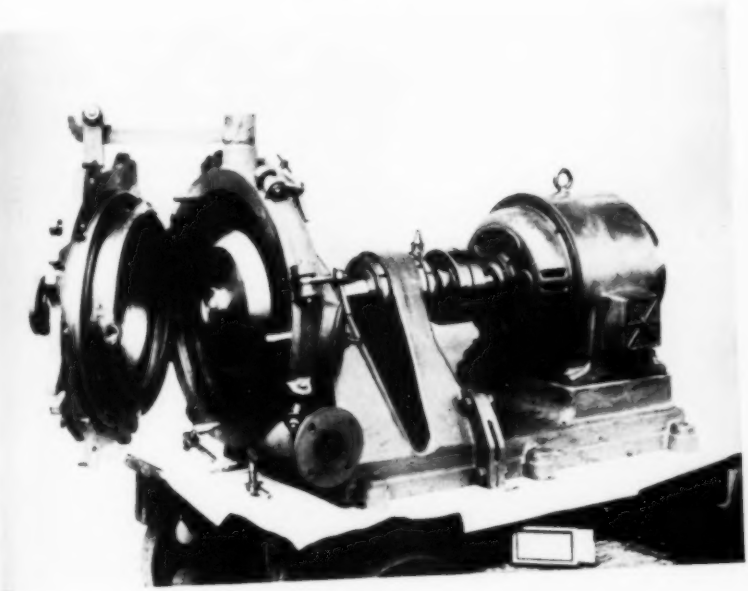

FIG. 2.
PREMIER MILL.

[*To face p.* 534.

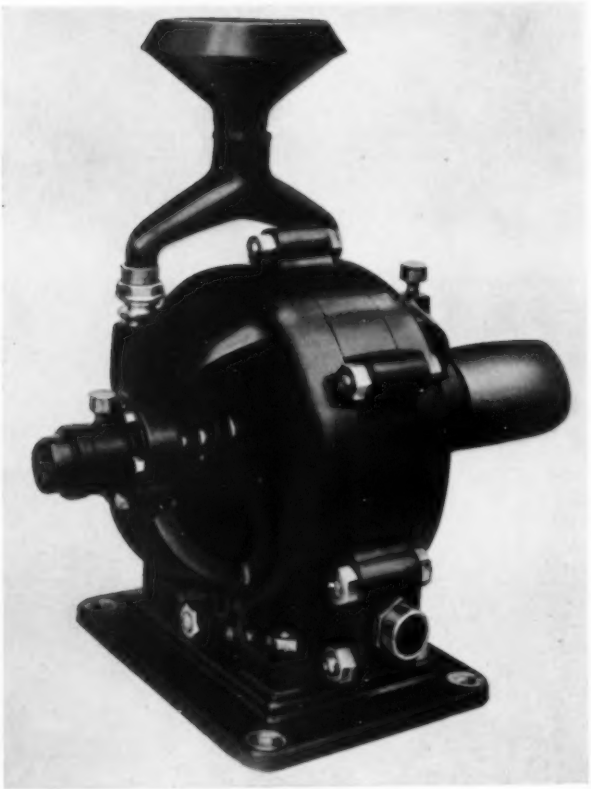

FIG. 3.
HATT-DUSSEK MILL.

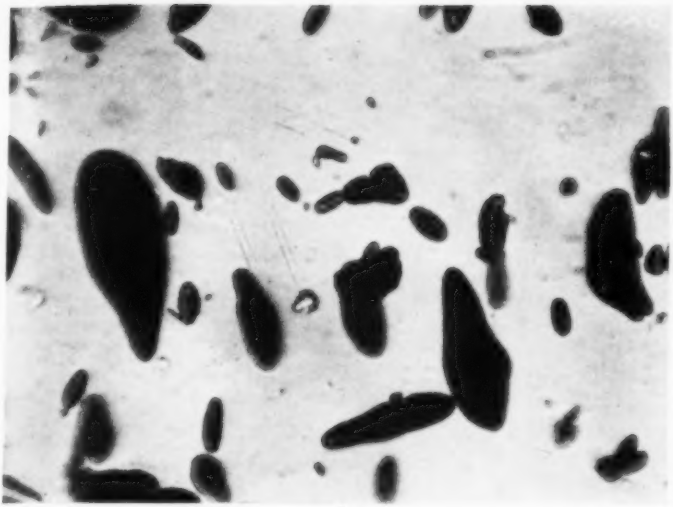

FIG. 10.

PHOTOMICROGRAPH OF TYPICAL INDUSTRIAL STABLE EMULSION, PRODUCED WITH BENTONITE EMULSIFIER. MAGNIFICATION ×900.

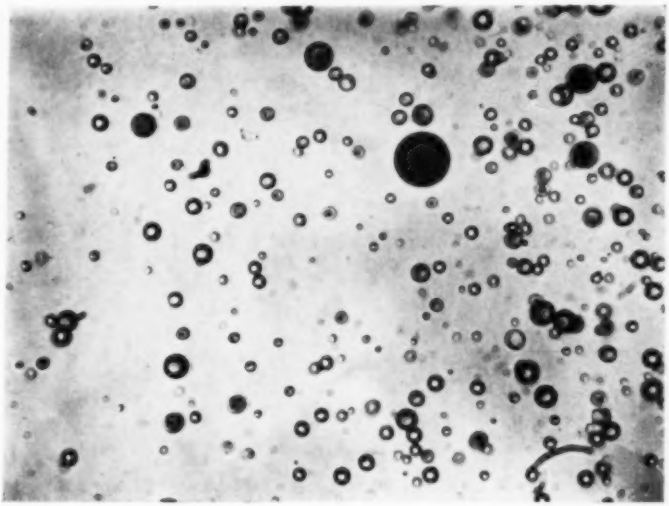

FIG. 11

PHOTOMICROGRAPH OF TYPICAL BITUMINOUS ROAD EMULSION. MAGNIFICATION ×775.

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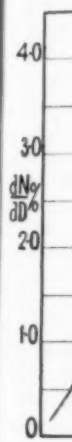

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production of improved dispersions or, possibly, as possessing higher rates of throughput than their competitors. In making comparisons of this sort, it is almost always found that the results have been arrived at without adequate control of all the operating factors. It is, of course, quite possible to take a given mill—say the Hurrell—and to open up the gap setting to a figure two to three times greater than normal, and then to show a considerable reduction in power consumption. If, however, the emulsions so made are tested quantitatively for dispersion, it will often be found that, beyond a given critical setting of the gap, the dispersion falls away, so that this must be taken into account in evaluating the effect on power consumption. It will also be found generally that at slower speeds of running the dispersion falls away, so that power consumption in this direction must be considered in the light of the dispersion produced, and the same is true in measuring throughputs.

In the author's experience, the advantages and disadvantages of the various well-known mills are to be found in such points as convenience of layout and adjustment, rather than in any definite positive advantage in either the dispersion produced, the power consumption required, or the rate of throughput maintained.

As regards the influence of gap setting, the following curves are of interest :—

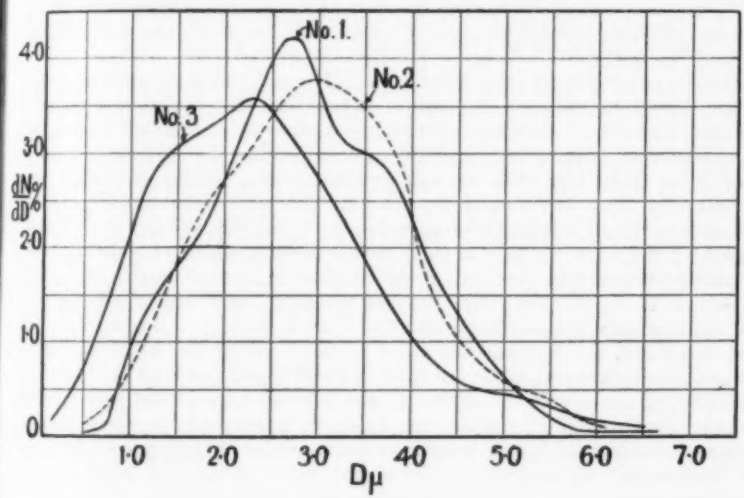

FIG. 4.

Curve No.	1.	2.	3.
Rotor size, in.	12	10	12
Speed, r.p.m.	2992	2986	2990
Gap, in.	0·020	0·014	0·015

Curves 1 and 3 are strictly comparable, being from emulsions made on mills of the same size. Curve 2 is of interest as showing the effect of using a

similar mill but fitted with a smaller rotor, running at a similar speed. In other words, we have here the effect of the reduction of peripheral speed due to the smaller rotor. The gap setting is almost identical with that of Curve 3.

Research Development.

We have, so far, discussed the development in methods of manufacture from the earliest commercial stages to the present day, and it has been assumed throughout that the product has remained more or less the same. This is, of course, not true, and hand in hand with advances in plant and installation technique, aimed at more convenient and economical operation, there have gone the improvement of plant from the point of view of getting a more meticulous control over the product and, in many cases, of introducing into the formulæ new ingredients and reagents for the production of the emulsion, so that it should possess a different and more definite range of properties in use than could have been contemplated at the beginning, in the absence of much theoretical knowledge of the constitution of the emulsions. It is not an exaggeration to say, in fact, that the progress achieved in the quality of emulsions from, say, 1925 to the present day represents the difference between a usable but rough-and-ready article, and a precision product which is controlled at least as accurately as any other material supplied in similar bulk on the commodity market to-day.

Let us cast our minds back to the state of knowledge of the constitution of the ultimate product in, say, the year 1925, in which the author first joined this particular industry. The first and ever-present problem at that time was as to whether emulsification would proceed normally on any given day. Variations were found, usually, as has been stated, not of a serious extent, almost every few days on which manufacture was carried on and, as a general rule, nothing but empirical explanations for the changes observed could be hazarded. The second problem was: having produced an apparently satisfactory emulsion—and by this was meant nothing more than that it had a lightish-brown colour and could be rubbed out on the palm of the hand to give a good sticky coating which was difficult to remove—would this product, of which there might be anything up to 100 tons in the storage tanks, stay as emulsion, or would it collapse, or would it change from a fluid product to a thick cream? All being well up to this point, we then had the third problem, which was as to whether, when the product arrived on the road, it would break and bind as it should. Finally, although this seemed to be rather in advance of our capabilities at this time, we did wonder why the emulsion, as originally prepared, sometimes came out thick and sometimes came out as of watery consistency. I shall endeavour to give you, in as few words as possible, some of the answers which we subsequently found to these various queries.

To begin with the question of irregular emulsification: at that time we did not know that different types of bitumen were different as regards emulsification. They gave the correct penetration and, within limits, the right melting point and ductility, and, on rare occasions when we estimated the percentage of asphaltenes, no surprises were forthcoming, although we knew that the percentage of asphaltenes varies from one crude to another. None of these tests seemed to furnish any reason for expecting differences in

emulsification behaviour. At a comparatively late stage in the development we began to be aware of the importance of the acidic constituents of the bitumen, and this certainly gave us a clue to a good deal of what was happening in the mixer processes. Even to-day, however, as regards the behaviour of a given bitumen under a given emulsification process, we cannot do more than say that it is entirely specific. We may hazard a guess that with a given bitumen a preponderance of a given wax may unfavourably influence its reaction to emulsification, but we are moderately well convinced that if the action is to be traced to such a constituent as wax it is only indirectly so traceable. In the author's laboratory at that time we tried to solve the problem by investigating the emulsification behaviour of large numbers of pure chemical substances.

These were emulsified in a Hurrell mill, using 1·5 per cent. potassium oleate solution. In all cases equal volumes of 1·5 per cent. potassium oleate and the compound in question were passed through the mill and then remilled *once*. The type of emulsion was determined in each case and the dispersion examined qualitatively. The results are summarized in Table I.

The following relationships appear to hold with regard to the compounds given in Table I :—

(*a*) *Benzene* gives an oil-in-water emulsion of fine dispersion and high stability.

TABLE I.

No.	Compound.	Emulsion Type.	Dispersion and Stability.
1	Benzene	O/W	Fine, stable.
2	Toluene	Dual	,, unstable.
3	Xylene	W/O	Medium, stable.
4	Mesitylene	W/O	,, ,,
5	Ethylbenzene	Dual	Similar to toluene.
6	Butylbenzene	Dual	,, ,,
7	Nitrobenzene	O/W	Fine, stable.
8	Nitrotoluene, *o*- and *m*-	O/W	Medium, stable.
9	*p*-Nitro-*m*-xylene	O/W	Fine, stable.
10	2 : 4-Dinitro-*m*-xylene	O/W	,, coagulated on standing.
11	*m*-Nitromesitylene	O/W	,, stable.
12	Chloroform	O/W	Fine, stable.
13	Bromoform	O/W	,, ,,
14	Carbon tetrachloride	W/O	,, ,,
15	Carbon disulphide	W/O	,, ,,
16	Ethyl ether	O/W	,, ,,
17	*n*-Pentane	O/W	Fine, stable.
18	*n*-Hexane	W/O	Medium, stable.
19	*n*-Heptane	W/O	Fine, stable.
20	*cyclo*Hexane	O/W	Fine, stable.
21	*cyclo*Hexanol	O/W	,, ,,
22	*cyclo*Hexyl chloride	O/W	Coarse, unstable.
23	Naphthalene	O/W	Fine, stable.
24	Tetrahydronaphthalene	O/W	,, ,,
25	Diphenyl	O/W	,, ,,
26	Chlorbenzene	O/W	Medium, stable.

(*b*) *The progressive substitution of methyl groups* to give toluene, xylene, and mesitylene causes the emulsion type to change over to water-in-oil, passing through the intermediate stage with toluene, which forms a dual emulsion.

(*c*) *Substitution of other alkyl groups* (nos. 5 and 6) has a similar effect.

(*d*) *The strongly positive nitro-group* leads to oil-in-water emulsions (nos. 7–11), one nitro-group being sufficient to counteract the reversing influence of two or three methyl groups (nos. 9 and 11).

(*e*) *Substitution of halogens* in the benzene (chlorobenzene, etc.) does not alter the emulsion type, but leads to coarser dispersion.

(*f*) *The aliphatic compounds*, nos. 12–16, suggest that the more polar molecules tend to give oil-in-water emulsions.

(*g*) *The homologous series*, nos. 17–19, shows a progressive change in emulsion type and stability with increasing chain-length; long chains tend to give water-in-oil emulsions.

(*h*) *The cyclic compounds*, nos. 20–25, all give oil-in-water emulsions.

(*i*) *Substitution of halogens in the case of cyclic compounds* does not change the emulsion type, but leads to coarse and less stable emulsions than in the case of benzene—compare nos. 22 and 26.

These somewhat general effects of constitution on emulsification, by the process previously described, could not be correlated with surface tension or interfacial tension relationships, and the problem was complicated by the fact that many of the compounds tended to abstract a proportion of fatty acid from the emulsifier solution during emulsification, the latter then becoming alkaline.

Further interesting results were obtained with mixtures of compounds which individually gave opposite types of emulsions. These are shown in Table I*a*.

TABLE I*a*.

No.	Mixture.	Emulsion Type.	Dispersion and Stability.
27	Benzene-xylene, 75 : 25	W/O	Coarse, rather unstable.
28	,, ,, 85 : 15	W/O	,, unstable.
29	,, ,, 96 : 4	O/W	,, ,,
30	Benzene-hexane, 88 : 12	W/O	Coarse, unstable.
31	,, ,, 94 : 6	O/W	,, ,,

(*j*) *Table Ia* shows that an oil giving water-in-oil emulsions has a marked effect when added even in quite small amounts to one giving oil-in-water emulsions. Thus, as little as 4 per cent. of xylene is sufficient to prevent benzene from forming its usual fine oil-in-water emulsion and 15 per cent. of xylene is sufficient to cause reversal. Similar effects occur on adding hexane to benzene.

(*k*) *In Table I* it was seen that the longer-chain aliphatic compounds formed water-in-oil emulsions, and following the indication of (*j*) above, it was thought that aliphatic compounds such as wax might have a marked influence on the emulsifying properties of bitumens. Investi-

gation showed that up to 10 per cent. of soft paraffin wax could be added to 300 penetration Venezuelan bitumen without appreciably affecting the dispersion obtained on emulsification in the mill with 1·5 per cent. potassium oleate. With 10 per cent. of hard wax (m.pt. 57° C.) the emulsion became definitely coarse, however, and 15 per cent. of the wax caused instability. With higher amounts of soft wax (up to 20 per cent.) rather coarse, but fairly stable emulsions were obtained. These were particularly interesting, since the emulsion particles were irregular in shape, instead of being spherical, presumably owing to crystallization of the wax. The experiments failed to show any correlation between the normal wax contents of bitumens in general use and the emulsification properties of the bitumens.

It will be seen that although these rather vague correlations may perhaps be observed, the specificity of the emulsification phenomenon remains largely where it was. Undoubtedly the substitution of mechanical means of emulsification, such as the colloid mill, does aid in producing emulsion of very regular, sound quality from a wide range of types of bitumen, but it cannot really be said that emulsification properties of a given bitumen can yet be predicted from any series of simple tests, and it should be emphasized that the properties of the given bitumen in one process of emulsification are not necessarily duplicated in any other. This is the fundamental mistake which is being made in certain countries where efforts are being directed to producing a test for emulsification as a guarantee of the suitability of supplies of bitumen for this process. The tests can have value, in the last resort, only if they are made by every process of emulsification used in the country where the bitumen is being supplied. It is not sufficient to emulsify the bitumen under test, say, by passage through a Hurrell mill, and then to imagine that when emulsified by some form of mixer process it is sure to yield equal results.

As a matter of interest on this point, reference should be made to Fig. 5, which shows the size/frequency curve of a typical emulsion of 200 penetration Mexican bitumen, with a similar curve derived from the same type of bitumen, but using a variant of the Montgomerie process, with a slow-stirring mixer.

It will be seen that although the two curves show variations of shape and uniformity, there is no striking difference in the general dispersion.

Let us now turn briefly to the second problem which engages the manufacturer of bituminous emulsions: to wit the storage stability of his product. Having got the emulsion into the storage tank, it may change its state, due to two fundamental processes: first, simple sedimentation, and secondly, some process of flocculation, which may eventually lead to complete coagulation of the disperse phase.

Taking the second alternative first, as being the less usual, it can be said that complete coagulation of an emulsion of bitumen, known to be capable of successful emulsification, must always be due to some error in the type or concentration of emulsifier used or to some mechanical fault in the process. A reservation has to be made on this observation, regarding the known susceptibility of the bitumen to emulsification, because there are certain physical and chemical characteristics of certain types of bitumen which

preclude their emulsification or preclude the storage stability of their emulsions, once formed. I need only mention, in this connection, the influence of high specific gravity of the bitumen. We shall consider the normal effect of the difference in specific gravity of the bitumen, and that of the aqueous phase, when we come to sedimentation, but for the moment I

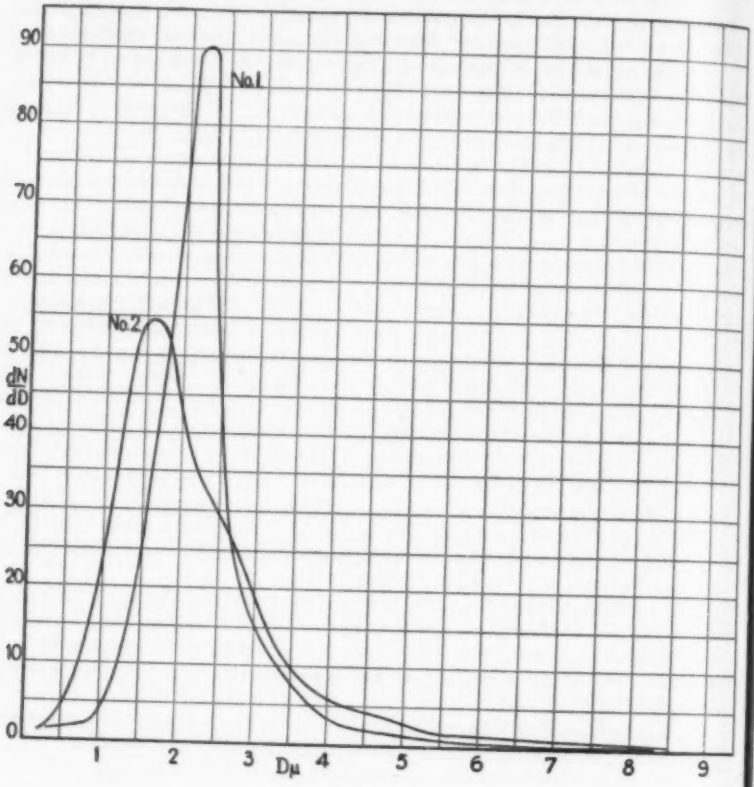

FIG. 5.

SIZE/FREQUENCY CURVES OF MONTGOMERIE AND MILL EMULSIONS OF 200 PENETRATION MEXICAN BITUMEN.

Curve No. 1. Montgomerie emulsion, laboratory mixer.
Curve No. 2. Mill emulsion (1% sodium oleate), laboratory mill.

would refer to a bitumen having a really high specific gravity—say 1·06 or over. It is found that with such bitumens, unless some step can be taken to raise the specific gravity of the aqueous phase, so reducing the difference in specific gravity between the two phases, ready coagulation of the disperse phase will be experienced. This seems to be due to the fact that not only is the initial sedimentation heavy, but when packing to a dense

formation of particles occurs at the bottom of the sedimenting column of liquid, there is always a very high pressure developed at the points of contact between superposed spheres of bitumen. This high pressure naturally tends to force out the adsorbed film of emulsifier, which keeps the particles from coalescing normally, so that the greater the pressure so exerted, the more likely becomes the coalescence of the particles in contact. It is, in fact, very well marked in various types of bitumen which have been investigated.

It is also possible to get this coagulation of the emulsion in the case of very concentrated emulsions—say with a bitumen content of more than 70–75 per cent., when the particles of the emulsion become so tightly packed that they commence to deform in the bulk of emulsion, merely due to the contact pressures between them. It is not infrequent to find the whole system set up to a sort of gel, which is not able to disperse again, except by re-submission to the emulsification process.

As has been said, however, these cases of coagulation are rather rare in the case of bitumens normally found satisfactory for emulsification.

The second type of phenomenon which may occur in storage is, as has been stated, simple sedimentation. The factors governing sedimentation are normally given, in the somewhat loose way common to text-books, as those entering into Stokes' Law, as follows :—

$$6\pi\eta rv = \tfrac{4}{3}\pi r^3(d_1 - d_2)g$$

where η = the viscosity of the aqueous phase.
r = radius of the falling particle.
v = velocity of the fall of the particle.
d_1 = density of the particle.
d_2 = density of the aqueous phase.
g = gravitational constant.

In fact, however, Stokes' Law cannot be directly applied to common bituminous emulsions in the ordinary sense. The reason for this is that Stokes' Law presupposes that the particles of disperse phase are free to fall through the continuous medium uninfluenced by each other or, of course, the walls of the vessel. In the case of an emulsion with a concentration of disperse phase over about 50 per cent. by volume, there can be no question of free fall of the particles, and, in fact, investigations of what really happens in a sedimenting column of emulsion of this concentration show that the phenomena are rather complicated. What happens is that the whole bulk of the particles tends to fall together, or, as it might alternatively be expressed, the continuous medium tends to slip through the mass of particles and to come to the surface. The mass of particles concentrates towards the bottom with gradual packing of the various sizes into the closest spontaneous arrangement. After a little while, therefore, you get in the sedimenting column a thin layer of more or less pure aqueous phase and, below that, a layer of almost constant concentration, as we go downwards, of all sizes of particles, with the proportion of large ones tending to become greater towards the bottom, and finally a packed layer of particles at the bottom. The following curve was determined for an emulsion of Texas bitumen in 1·5 per cent. potassium oleate, allowed to sediment in a

cylindrical column 80 cm. in height, 4 cm. in diameter. It shows the *disperse phase* concentration at varying heights; owing to the high water absorption of the bitumen, it would not have been satisfactory to plot bitumen content against height.

From the practical point of view, this can be overcome by arranging that the storage tanks shall have fitted to them a pipe system, which enables the

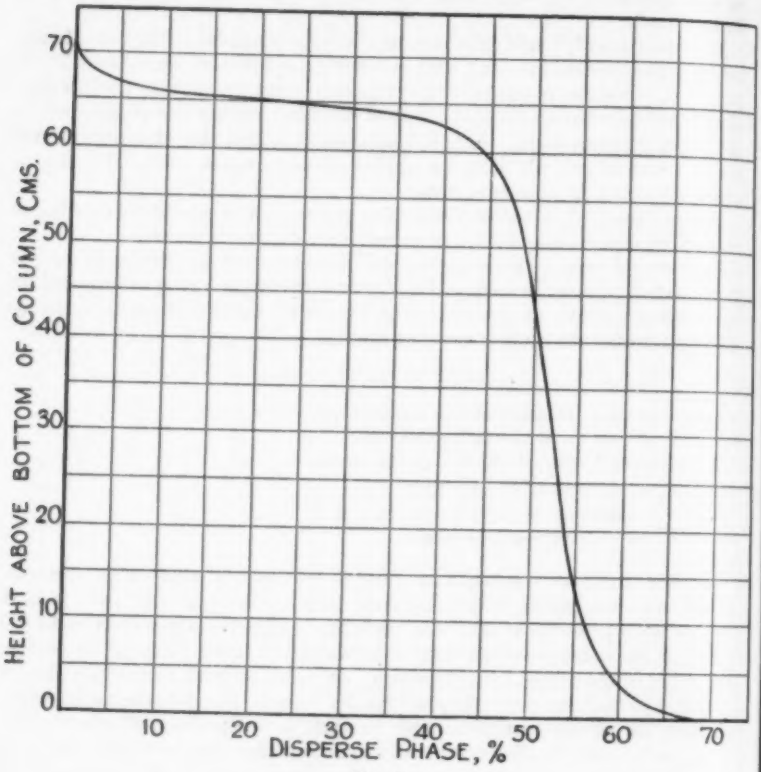

FIG. 6.

SEDIMENTATION OF CYLINDRICAL COLUMN OF EMULSION—DISPERSE PHASE CONCENTRATION AT DIFFERENT HEIGHTS ABOVE THE BASE.

contents to be circulated by pumping at regular intervals. In this way the bottom packed layer can be re-distributed in the more rarefied emulsion at the top of the column, before it is so tightly packed that it can no longer be handled.

If the emulsion has been decanted off into drums or other containers, then the only means available are the stirring or rolling of the containers. It is when the question of stirring a sedimented container of emulsion arises that we come across some of the most interesting phenomena in the packing of

particles. With certain types of emulsion the sediment at the bottom acquires most peculiar properties and, in particular, it is possible to show, with certain stable emulsions, a very pronounced " paste effect ", which is sometimes inaccurately referred to as anti-thixotropy. If the sediment is separated out and poured gently from one container to another, it appears to have the consistency of a very thick cream. If, however, an attempt is made to pour it quickly, it sets solid and will not leave the first container. It is also possible to take this apparently fluid sediment and to subject it to a sharp shearing force, when it will set solid : as, for instance, when a glass rod is jammed into a beaker containing the sediment. The reason for this behaviour lies, probably, in the changes of the configuration of packing which occur when the spontaneous arrangement of the particles is disturbed ; it bears a relation to the effect observed when wet sand is displaced on the sea-shore, and is undoubtedly connected with the phenomen of dilatation. The practical significance of this is that, with the types of emulsion which show this behaviour at its most marked, it may become virtually impossible to stir up a sediment which has accumulated over any length of time. Certain emulsions made with protein emulsifiers show this behaviour very strongly, and it is, in fact, frequently experienced when these emulsions are returned by the customer as containing lumps of coagulated bitumen, that, in fact, the lumps or bitumen layer in such cases may consist of very heavily sedimented emulsion, which can only be re-dispersed with great care. With the normal soap-type emulsions used for the bulk of the work, however, the sediment may, in certain circumstances, become rather stiff for manipulation, but generally it is possible to re-distribute it by stirring or rolling.

The next problem which we always have before us is the question of the road performance of the emulsion. At this stage we confine the discussion to road emulsions, but it should be understood that most of the physical properties so far described are possessed in various degrees by all types of emulsion with a bituminous base, even though designed for other purposes, and later on it is proposed to devote a few remarks to these special emulsions.

In the early days of emulsion manufacture it was assumed that once a satisfactory emulsion had been made, its road performance would be equally satisfactory, and it took quite a little while to appreciate that an emulsion which is good *qua* stability and dispersion may be quite unsuitable for the purpose for which it is designed. It was not realized by what process the emulsion actually set on the road, and there was much talk of emulsions " throwing off " their water, as if the process were an active operation on the part of the emulsion, rather than a passive submission to various factors bringing about setting. In fact, of course, an emulsion does not throw off its water : the water leaves the disperse phase by a series of perfectly familiar physical and chemical processes. In recent years these have been investigated in great detail, and our understanding of the processes of breakdown of emulsions, though still incomplete, enables us to get a very good picture of what happens. The mechanism of break of emulsion may be divided into three main headings :—

1. Evaporation.
2. Chemical Coagulation.
3. Capillary Effects.

1. *Evaporation.*

Generally speaking, in road work or, for that matter, in most industrial applications of emulsions, the bulk of the water is lost by evaporation pure and simple. This evaporation follows very much the same laws as the evaporation of water from a free surface, and it can be seen by reference to

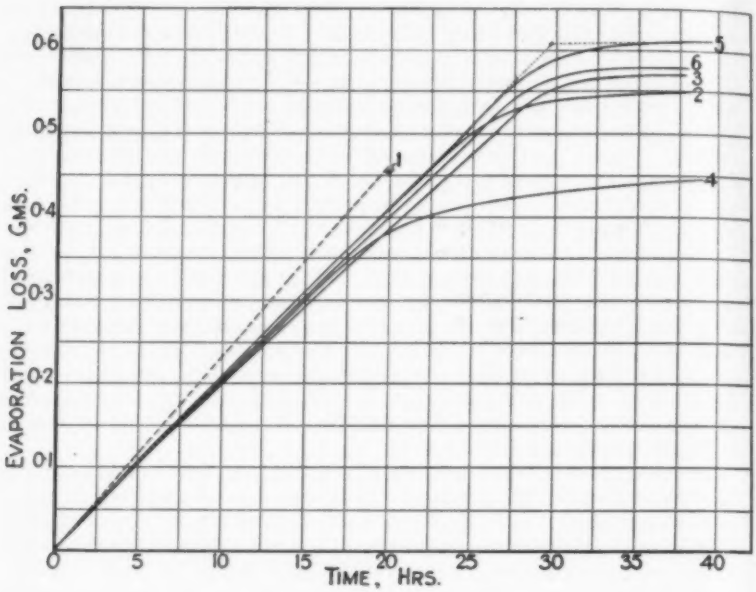

FIG. 7.

INITIAL RATE OF EVAPORATION FROM EMULSIONS.

(Loss in weight *v.* drying time.)

(Film area = 12·9 cm. Temperature = 21·5° C. Relative humidity = 80 per cent.)

Curve No. 1. Distilled water.
" 2. Labile emulsion A.
" 3. " " B.
" 4. " " C.
" 5. Semi-stable emulsion.
" 6. Stable emulsion.

Note that all the emulsions lose water at a slightly lower rate than distilled water, owing to the dissolved solids in the aqueous phase. The effect is particularly marked in the case of Labile emulsion C which contained an exceptionally high percentage of electrolyte. The initial rates of evaporation are constant for about twenty hours.

Fig. 7 that over quite a range of emulsions, the initial rates of loss of water by evaporation, under constant external conditions, are the same. At a later time in the setting of the emulsion a point is reached at which a sudden change comes over the rate of evaporation, due to the inhibiting effect of the residual magma of bitumen. The point at which this occurs differs to quite

a considerable extent among different emulsions, and this is exemplified in Fig. 8.

It is interesting that the position where this rapid change takes place has been proposed as a fundamental characteristic of road emulsions by the Société Chimique de la Route in France. There are several objections which can be made to the employment of this characteristic as a guide to performance, but there is no doubt that it has its theoretical interest.

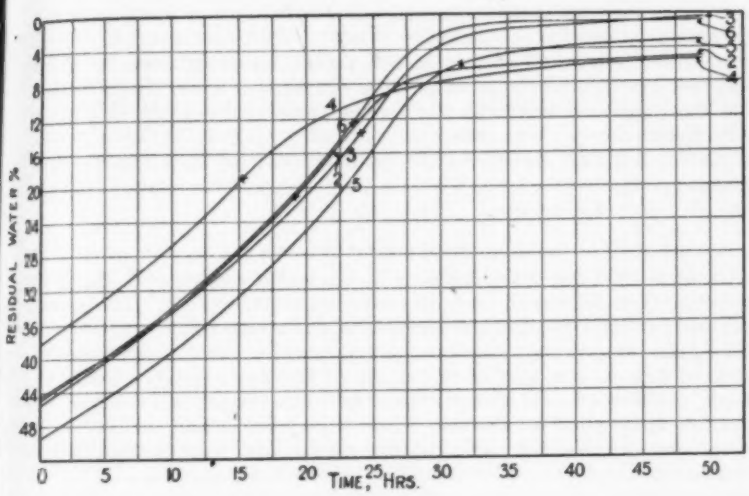

FIG. 8.

EVAPORATION OF WATER FROM EMULSIONS.

(Residual water content *v.* drying time.)

(Film thickness = 1 mm. Temperature = 21·5° C.
Relative humidity = 80 per cent.)

Curve No. 2. Labile emulsion A. Lability = 21·3.
" 3. " " B. Lability = 13·7.
" 4. " " C. Lability = 18·8.
" 5. Semi-stable emulsion. Lability = 6·8.
" 6. Stable emulsion. Lability = 12·6.

Curves show *percentage residual water content* plotted against drying time. Conditions as above.

Note that the initial evaporation when plotted in this way is not linear, but slightly convex to the time axis.

In actual road work, however, it is uncommon for the evaporation of the water to be able to proceed in a quiescent manner. Normally the application of the emulsion is followed by the scattering of stone chips over it, and these are then rolled, or possibly immediately opened to the passage of traffic. In any case, the application of the chips themselves and the action of passing vehicles, or of the roller, are sufficient to disturb the evaporating film mechanically. This has been found to produce an interesting effect on the point at which the bituminous magma ceases to be a collection of

packed, isolated particles and commences to assume the properties of adhesive bitumen. This point, of course, is usually referred to as the point of break of the emulsion. It does not mean the point at which an anhydrous film of bitumen is obtained—and different emulsions yield bitumens which commence to show adhesive properties at different residual water contents—but, generally speaking, there is a fairly considerable amount of water remaining in the film at the point at which the normal bulk properties of bitumen begin to be manifested. The point at which a substantial coagulation of the bitumen is first observed under conditions of mechanical disturbance may be called the "Lability Point." We shall discuss this further later in the paper. The effect of the mechanical disturbance, to which reference has been made, is to produce coagulation at an earlier stage: that is, at a greater residual water content than would be the case if the evaporation were entirely quiescent. Referring back to Fig. 8, the points marked with crosses show the lability points for the emulsions the curves of quiescent evaporation of which have been traced, and the relation between the two can readily be seen.

2. *Chemical Coagulation*

In the normal use of the emulsion it comes into contact with the stone surface of the road and also with the newly applied chippings. These stone surfaces are found to exert a breaking influence on the emulsion. In other words, if a chip is suspended in emulsion, it will be found, after a certain lapse of time, that a coating of coagulated bitumen is present round the stone. It was at first thought that this phenomenon was due to the presence of coagulating substances in the stone, such as lime salts or soluble calcium compounds. Investigation has shown, however, that the effect is by no means so simple, and what really takes place is that soap and alkali are adsorbed on to the surface of the stone. In this connection it should be realized that although most stones do not possess any marked porosity in the ordinary sense, they do undoubtedly possess a micro-porous structure, and, therefore, the extent of the coagulating surface of the stone may be very much greater than the mere external surface presented to the eye. Stones vary greatly in their power to coagulate given emulsions, and, what is more, if a series of emulsions is placed in a certain order of stability, when submitted to the coagulating action of a given stone, it will frequently

TABLE II.

Aggregate.	Percentage of Bitumen Coagulated.		
	Types of Emulsion:		
	Labile.	Semi-stable.	Stable.
Arnold's limestone	8·4	5·5	1·7
Mountsorrel granite	9·0	4·2	1·8
Craig yr Hesg Sandstone	25·3	10·9	2·3
Llandebie Limestone	4·1	—	—
Alderney Granite	10·6	—	—
Wickwar Limestone	15·0	—	—
Forest Rock Granite	16·5	—	—
Llanbedrog Granite	20·7	—	—

be found that by substituting another stone, even when it is of similar general reactivity, the emulsions are frequently placed in quite a different order of stability. The effect, therefore, is quite specific, and may be due to a combination of the chemical nature and reactivity intrinsic to the given stone surface and the dimensions and extent of the micro-pores. Table II shows typical coagulations with emulsions belonging to the three main categories—labile, semi-stable, and stable—with a variety of British road stones.

It will be noted that the variations in coagulative power of the different aggregates are so great that the range of coagulations produced, as between the labile surface-dressing-type emulsion and the semi-stable emulsions which are normally prepared with much higher concentrations of soap, overlap. This is not so evident with the results with stable emulsions, which are not normally affected to anything like the same extent by the stone, and may, in general, be said to be almost completely immune to this coagulating effect.

3. *Capillary Effects.*

This factor was, at one time, thought to be very much more important than is now held to be the case. It will readily be recalled how, in earlier days, the so-called filter-paper test was used as a guarantee of quality of road emulsions. This test was supposed to demonstrate the rate of break of the emulsion; in fact, of course, it did nothing of the kind. All that happens when a drop of emulsion is exposed on filter paper, at any rate for the first five or ten minutes, is that a certain amount of aqueous phase passes out from the central drop into the pores of the paper, due to the capillary forces acting in the fine capillaries. This effect is duplicated, to a certain extent, on the surface of the road, as many road surfaces are either directly porous, as in the case of water-bound roads, or contain a percentage of dust or other fine material, which serves as a species of blotting-paper for the aqueous phase of the emulsion. As a means of reducing the water content, porosity is very much on an equal footing with quiescent evaporation; it separates the water, and the residual bitumen assumes its adhesive state at a time dependent on the characteristics of the original emulsion and on the presence or absence of mechanical disturbance. There is this difference in theory: when the water separates, due to porosity, it carries with it the emulsifying agent, whereas when it evaporates, the emulsifying agent is left behind, and in most cases will cause some retardation in the appearance of coagulation. It is interesting, from the point of view of road construction with emulsions, to discuss the relative importance of the three different main influences which have been enumerated. The problem is, however, very complex, because the rate of evaporation depends on many circumstances, but, in the first place, on the ambient temperature and on the wind velocity at the road surface. Secondly, the degree of mechanical disturbance can never be predicted, and this in turn will have an influence on the rate of coagulation, due to the mechanical disturbance factor. The degree of coagulation due to the stone aggregate depends, of course, on the type of stone, the specific stability of the emulsion to that stone, and, as a practical factor of great importance, on the amount of stone and the amount of surface of that stone exposed to unit quantity of emulsion on the road.

In general, however, an analysis of the normal incidence of these factors leads to the conclusion that the first factor, sometimes referred to as the lability factor, is normally at least as important as the chemical factor, and the porosity factor, in these days of re-treatment of already bituminized roads, is of subsidiary importance. In cases of favourable weather conditions it is easy to see that the lability factor may have an altogether preponderatingly important rôle in producing the final result.

Viscosity of Emulsions.

When allusion was made to the early difficulties encountered, due to a change of bitumen type, it was indicated that one of the chief difficulties introduced with the new type of emulsion was its lower viscosity. At that time there had been small opportunity of giving detailed attention to the influence of the viscosity of the emulsion on its road performance, but a little fundamental thinking soon rendered it evident that this was, in fact, a very important characteristic. Normally, the road surface has a certain camber, and this causes any fluid liquid applied to the crown to tend to run down into the gutters. The less viscous the liquid, the more chance it will have to run away off the effective road surface, before it is covered with chippings or otherwise prevented from doing so. Furthermore, if the emulsion is too viscous, the minimum quantity which can be applied to a given unit of area is reduced and, therefore, its covering capacity may easily overstep that quantity which corresponds to the amount of bitumen necessary to bind the chippings without the presence of excess. Excess, of course, manifests itself sooner or later, by the fatting up of the surface, due to the rise of the bitumen under the pressure of the traffic, until it partly or completely engulfs the stone, which should form the running surface.

Viscosity control, therefore, is obviously important. Once this point had been reached, the next step was evidently to produce emulsions of a range of viscosity found by experience to be the best, as being the mean between the two undesirable consistencies mentioned above. The precise value of this mean is, of course, a matter of opinion, but there is a good deal of experience to show that for normal working in British conditions, and especially in this connection, when used as a surface-dressing emulsion, the figure should lie between 10° and 12° Engler at 20° C. A good deal, however, depends on the precise technique adopted by the workmen responsible for using the emulsion, and a gang trained to use a thinner emulsion could probably produce a good result with an emulsion of 5–6° Engler. Nevertheless, in the view of the author, 10–12° Engler constitutes the best general range to adopt.

It was known at an early stage in the manufacture of emulsions that the most straightforward way of producing emulsions of greater viscosity was to increase the bitumen content. The way in which viscosity rises with increasing bitumen content is shown in Fig. 9, curve 1. It will be seen, in particular, that above a bitumen content of 55 per cent. or so, the slope of the curves rises steeply and, in other words, above this figure great increases in viscosity result from small increases in bitumen content.

However, it was not possible to consider a variation in bitumen content as a final solution of the problem of producing emulsions of varying viscosity, because if any degree of precision is to be obtained in apportioning the

quantity of emulsions used to the area of road treated, it is necessary to have an emulsion of standard bitumen content. The problem was, therefore, a rather more difficult one to solve: that is, the increase or decrease in viscosity had to be produced at a given bitumen content. In order to solve this problem, research work was done to trace the origin of the variations in viscosity at given bitumen contents, found in passing from one type of bitumen to another.

In curve 2 it will be seen that the slope is more gradual and, further, that at any given bitumen content the actual viscosity is lower. At first it was thought that the differences experienced might have something to do with the amount of soap adsorbed from the aqueous phase on to the

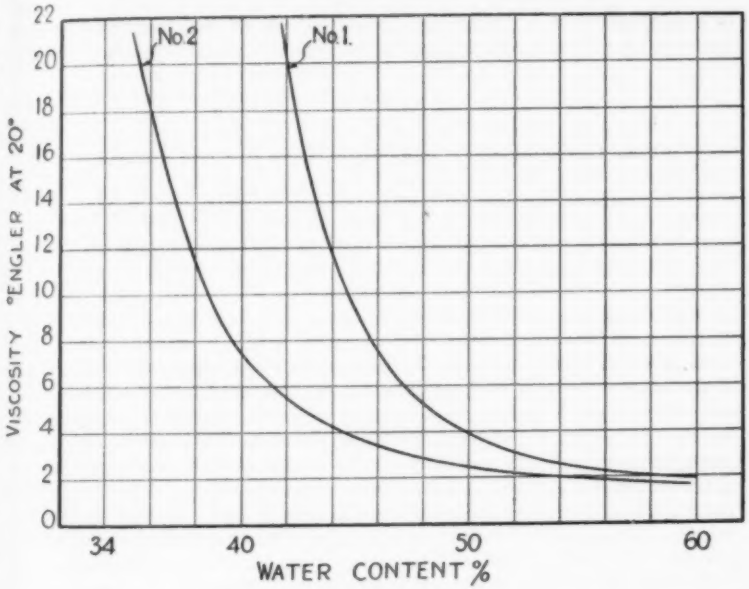

FIG. 9.

VISCOSITY/WATER CONTENT—CURVES OF EMULSIONS.

Curve No. 1. Water absorption = 24 per cent.
" 2. Water absorption = 12 per cent.

surface of the particles. When, however, careful measurements were made of the concentration of soap in the bulk aqueous phase, and from these a computation made of the amount adsorbed, a striking fact was found in the case of Mexican bitumen emulsion: the concentration of soap in the bulk aqueous phase was actually higher than the original concentration employed, and not lower, as would have been expected, had any considerable quantity of soap been adsorbed. This was true for emulsions made with both sodium and potassium soap. The actual concentrations found are shown in Table III.

What was the explanation of this? It at once leapt to the mind that in some way or another, as it was impossible for more soap to be present than was actually put in, the converse must be true and, in fact, a certain proportion of water had somehow become fixed, so that it did not function as part of the bulk aqueous phase. A lengthy series of experiments was carried out, which cannot be recorded here in detail, which resulted in the fact that this water was fixed by occlusion in the bitumen particles, and we finally succeeded in showing that this occlusion seemed to be, at any rate as a first observation, the result of the establishment of an osmotic equilibrium between the soap and electrolyte solution constituting the final bulk aqueous phase and the solution contained in the interior of the bitumen particles. This solution, therefore, must have acquired a certain content of osmotically active substances. Finally it was shown that the source of these substances was the presence of a minute amount of micro-crystals of

TABLE III.

Soap Concentration.	Soap Concentration in Aqueous Phase.	
Initial Emulsifier, % wt.	Sodium Oleate, % wt.	Potassium Oleate, % wt.
1·05	1·13	1·26
1·53	1·63	1·68
2·07	2·21	2·20

various water-soluble salts in the original bitumen employed. The effect of these micro-crystals of electrolyte (mainly sodium chloride) was to set up, as it were, a rather special type of semi-permeable membrane, constituted by the bitumen of the disperse particles. This semi-permeable membrane must be distinguished clearly from the ordinary Donnan membrane, in that, whilst the latter is permeable to certain ions, but impermeable to others, the present type of membrane is permeable to solvent, but not to solute. Bitumen is, of course, in bulk, one of the most water-impermeable substances known, but it can be shown that films of bitumen of minute thickness—say of the order one to two microns—do exhibit the permeability to water necessary to account for the establishment of this type of osmotic equilibrium.

We have, therefore, as the result of this work, the fact that the viscosity of this particular type of disperse system is governed mainly by the volume concentration of disperse phase. The difference between an emulsion of one type of bitumen and an equally concentrated emulsion of another type of bitumen, having a higher viscosity, is simply that the more viscous emulsion actually possesses a higher content by volume of disperse phase than the less viscous emulsion, this being due to greater swelling of the bitumen particles in the case of the more viscous emulsion, owing to the presence of water in the interior of the particles, due to the osmotic equilibrium.

Hatschek, in 1911, developed the following formula governing the viscosity of disperse systems:

$$\eta s = \frac{\eta}{1 - (\phi)\frac{1}{3}}$$

where ηs = viscosity of the disperse system.
η = viscosity of continuous phase.
ϕ = fraction of total volume occupied by disperse phase, where ϕ is assumed to be greater than 0·5.

Sibree and others have subsequently shown that if ϕ is substituted by $h\phi$, where h is a numerical constant for a given type of dispersion, this formula gives a good approximation to the observed results in many different kinds of systems. (In typical bitumen emulsions h shows values of the order of 1·3–1·6.)

Now that the phenomenon of water absorption has been demonstrated in bituminous emulsions of this type, it is possible to bring them into line with the Hatschek expression by interpolating the known percentage of water absorption to get the true percentage volume of disperse phase and, further, by interpolating a numerical factor $h = 1{\cdot}4$ or thereabouts, as has to be done with other types of disperse systems, when using the Hatschek equation. Subject, therefore, to the significance of this factor h being unravelled, it may be said that the Hatschek expression does give a good approximation to the viscosity of disperse systems, even though the viscosity of the disperse phase in these systems may vary from that of air, in the case of Sibree's froths, through that of liquid paraffin to that of the normally high viscosity of asphaltic bitumen of 200 penetration, or even higher.

Subsequently, this discovery has been used to work out a system whereby a bitumen deficient in water-soluble constituents capable of giving these viscosity increasing effects may have this deficiency rectified by the addition of further quantities of suitably dispersed electrolyte, and thus any bitumen may be treated to produce emulsions of any reasonable viscosity, at a chosen bitumen content. This principle has now been used in practice in the production of many thousands of tons of emulsion all over the world, and may be said to be a very typical example of the value of research, originally undertaken from a more or less abstract point of view, in developing an asset of considerable importance to the industry as a whole.

Applications of Emulsions.

Having surveyed some of the technical developments which have taken place in the technology of emulsions themselves (and it should here be emphasized that these are merely one or two typical examples of the increase in our knowledge since the early days of the industry), it is now proposed to indicate the manner in which the use of emulsions has developed during the same period.

It was made clear at the beginning that the first idea was to use these products as dust-laying compounds, and from this developed their use as surface-dressing binders. At the time that this development was taking place, grouting of packed stone courses with hot bitumen was a very common procedure, and yielded excellent results in the majority of cases. Here again, however, the difficulty of controlling the exact viscosity of the heated bitumen and of combating the chilling effect when the bitumen touched the road-stone led to difficulties of manipulation. When bitumen emulsion

became available, its great fluidity at once indicated it as a product which might be very well employed for the grouting or penetration process. Various adjustments of the working specifications had to be devised to ensure that penetration of the emulsion, while adequate, did not proceed to such an extent that it was able to run out underneath the layer of packed stone, and thus be wasted. This was, of course, achieved by placing a layer of sand below the stone and, in some cases, of working it up as a slurry between the stone, by rolling. A more economical form of grout was devised, usually known as semi-grout, which employed this slurry of sand in such a way that it filled approximately half the depth of the packed-stone layer, the emulsion being used for the remainder.

These processes—grouting and semi-grouting—continue to find employment, even to this day, and although supplanted on many of our main roads by still heavier constructions, due to the high demand of traffic in recent years, grouting and semi-grouting still form a very important item in those countries where the road system is being developed, in particular in some of the British Colonies.

When these processes had become established, a further development of the market took the form of an increased use of cutback bitumens, which, to a certain extent, supplanted emulsion in the form of coated stone carpets. Then, at a later period, these relatively coarse stone carpets were produced with finer gradings, and we now have quite a demand for what are known as fine carpets. These are materials of varying composition, but all adapted to present a final running surface with either a sand-paper texture or, in some cases, with a texture a little rougher than this.

Manufacturers of emulsion, therefore, began to look round for methods of entering into this market, and emulsions were developed, in the first place, for purposes of mixing, in suitable forms of mixer, with graded stone aggregates, to yield carpets similar to those prepared with cutback bitumens. It is rather curious that these carpets have never found any great application in Great Britain, but in other countries, notably in Germany and also, to a certain extent, in the United States of America and Canada, premix carpets and carpets mixed *in situ* on the road surface have developed to a large extent, and sales of emulsion for this type of work have extended greatly.

These emulsions are, of course, usually of the semi-stable type and, although similar in general properties to the labile emulsions which are used for surface dressing and grouting, have higher concentrations of emulsifier, usually of the soap type, and are thus adapted to the greater mechanical strains imposed upon them in the mixing operations.

Another type of emulsion which has more recently come to the fore, in connection with carpet construction, is a special type adapted for use as the tack coat which is normally applied to cause the fine carpet to adhere to the existing surface of the road, and to defeat any tendency there may be for the carpet to push under the roller or traffic. The problem in designing a tack-coat emulsion is that it should be capable of being brushed out to a very high rate of coverage without coagulating under the broom. This implies, of course, a certain amount of mechanical stability, which, however, must not be excessive, or the emulsion will not break quickly enough in unfavourable weather conditions to permit of the superposition of the carpet.

These two types of emulsion, however, have to yield pride of place, in the importance of the quantities sold, to what is known as the stable type of emulsion. These emulsions are so prepared that they have very high stability to mixing with stone aggregates and usually, though not necessarily, there is associated with this high mixing stability a high chemical stability. They can, in fact, be mixed with acids and electrolytes in moderate concentrations, without exhibiting coagulation. The great stability in mixing is used so that they may be incorporated with aggregates consisting largely of fine material. It is possible, for instance, to mix such emulsions, under suitable conditions, with soils, fine sands, fillers, or even with Portland cement. These emulsions first appeared on the market about 1928, and were used during that year for the preparation of soil/bitumen carpets on footpaths, playgrounds, and light-traffic surfaces. It is interesting to note that, even at that date, a considerable area of this type of mix was constructed at Croydon Aerodrome, and that this remained in position for quite a few years, until alterations in the airport caused the carpet to be abandoned. More recently this type of work, in which the natural soil, whatever it may be, is mixed with emulsions, with a view to producing a low-cost bituminized layer, which may form either the actual running carpet, when reinforced with a suitable anti-attrition layer, or, alternatively, may be used as the sub-foundation of a normal road construction, has come to the fore very much in this country, more particularly under the name of "soil stabilization." Actually, a good deal of confusion has, in the opinion of the author, been created by the indiscriminate use of this term, as between this form of bituminous mixture and the more general work on the study of soils, which has been carried out by Terzaghi, Hogentogler, and others. This work is largely devoted to analysing the characteristics of soils and to classifying them into various types, so that methods may be deduced whereby they can be rendered more suitable for supporting the actual running-carpet construction, which forms the useful surface of the road. These ideas may, of course, be applied quite generally, and the load to be supported need not be a traffic load at all, but a standing load, such as the weight of a building or other construction.

Now, one of the problems which has engaged the attention of these research workers on the stabilization of soil is the fact that only a certain number of soils are capable of sustaining any considerable load when exposed to the infiltration of water. Many of these soils are perfectly suitable at low water contents, but if more than a certain quantity of water is allowed to reach them, their bearing capacity falls sharply. If, therefore, means can be found to reduce the rate of infiltration of the water, certain soils, which otherwise would be unsuitable for employment to carry loads, except in the best drainage conditions, become more suitable, and this waterproofing effect may be obtained by using bituminous emulsion of high stability and mixing it with the soil. This is the proper employment of the term "bituminous soil stabilization."

Most of the work, however, which has been done in this country, and even in the United States, where the idea has received wide application, is not, strictly speaking, of this type at all, but consists in the employment of the soil as it is, or with the admixture of locally obtainable cheap aggregates, to produce a low-cost carpet, which has only to be finished with a stone

surface layer, to be able to withstand at any rate light traffic. This type of work is better referred to, for the sake of clarity, simply as "soil mix."

The present paper is not one in which the difficulties met with in the use of bituminous emulsion and soil can be discussed in detail, and for the moment all that need be said in this connection is that, in order to ensure a homogeneous mix of the stable emulsion with the fine aggregate, it is necessary to work in the presence of sufficient moisture to give the mixture a fairly damp consistency, as otherwise, even with these very stable emulsions, a certain amount of coagulation occurs, due to the intensive shearing of the disperse bitumen particles by the rubbing action of the aggregate particles in the mixing operation. It is, therefore, the practice to add water either to the emulsion or to the soil or to both, so that the final mix has a consistency such that, when tamped lightly, there is a just perceptible separation of water on the surface. If more water than this is present, no great harm is done from the coagulation point of view, but there is obviously the risk that dilute emulsion will drain away from the mix with the excess of water.

It is really quite surprising what can be done with suitable types of soil and very low final percentages of bitumen, when incorporated by the use of stable emulsions. With an aggregate, for instance, of the grading shown in Table IV, a mix completely stable to prolonged immersion in water may be

TABLE IV.

Passing	200	mesh	I.M.M.	6·1% wt.
,,	100	,,	,,	27·3 ,,
,,	80	,,	,,	12·3 ,,
,,	70	,,	,,	14·4 ,,
,,	50	,,	,,	10·7 ,,
,,	30	,,	,,	10·6 ,,
,,	20	,,	,,	5·3 ,,
,,	10	,,	,,	6·7 ,,
,,	¼″	,,	,,	6·6 ,,
				100·0 ,,

obtained, with the use of only 3 per cent. of bitumen. In actual fact, a portion of such a mix has been allowed to soak in the author's laboratory for seven years, and is still quite hard and difficult to cut with a penknife. This represents a particularly favourable soil, but with other types of soil similar degrees of waterproofness may be obtained—in some cases, however, only with the use of larger percentages of bitumen.

It will, of course, be understood that although this degree of mechanical stability persists after prolonged immersion in water, it is not possible for the very limited quantities of bitumen indicated completely to waterproof the mixed material. What happens is that the infiltration of moisture is retarded, but that at equilibrium moisture is present to an extent approximately equal to that necessary to fill the voids in the mix; but that the distribution of the bitumen throughout the mix has been effected to such an extent that the individual particles are sufficiently bound together, so that the general cohesion and stability of the mix are not affected by the presence of the water.

The addition of clay to mixes of this type is sometimes advocated, but it should be stressed that, in the case of mixes containing appreciable

percentages of true clay, the immersion in water of samples is usually followed by a pronounced loss of bearing capacity. This is due to the fact that the particle size of the clay is so fine that the binding power of the bitumen is inevitably small, and the capacity of the mixed material to withstand the action of water is, therefore, not great. So long as the mixes containing clay are not subjected to immersion conditions, however, and the access of water is only to a restricted extent, the great bearing capacity which may be attained in suitable circumstances, due to the addition of clay, may be an advantage. This type of mix, however, would seem not to be suited to conditions where water has to be reckoned with.

Industrial Stable Emulsions.

As has been stated previously in this paper, the bulk of consideration has been given to emulsions designed for road work. There is, however, another important sphere of use for bituminous emulsions for industrial purposes generally. These purposes include the preparation of insulating layers for the exclusion of moisture, the formation of compositions involving sand, cement, micro-asbestos, and other materials for heat insulation, electrical insulation, and similar purposes.

The type of emulsion used mainly for this work is, however, something quite different from those we have been discussing heretofore. These emulsions are usually prepared employing bentonite or some similar form of colloidal clay as the emulsifier.

Almost any type of bitumen may be emulsified with a suitable clay, provided that appropriate conditions are selected. The clay suspension to be used as the emulsifier is normally made up in a concentrated form at first, containing, for example, 15 per cent. of bentonite; the resulting high consistency facilitates dispersion of the clay. The suspension, or "clay slip" as it is called, is subsequently diluted to the required concentration and, when necessary, is flocculated to some extent by the addition of an electrolyte. The conditions in any particular instance have to be determined empirically, and depend on the properties of the clay and of the bitumen, as well as on the characteristics desired in the finished emulsion.

The manufacturing process normally consists in running the clay slip simultaneously with molten bitumen into a suitable form of mixer, which already contains some clay emulsion, the temperatures being adjusted so that the emulsion is produced at approximately the melting point (R. & B.) of the bitumen. For proper dispersion of the bitumen it is necessary to maintain a high consistency of the material in the mixer, since, to a very large extent, the emulsion itself is the emulsifying machine. In these circumstances the bitumen, which is added in a thin stream, is drawn out into thin threads in the clay suspension, and ultimately breaks up into cigar-shaped particles. The latter are stabilized by clay particles concentrated in the bitumen/water interface, and in a good emulsion retain their shape permanently, owing to the rigid nature of the clay films. The elongated particles characteristic of clay emulsions are shown in Fig. 10; the spherical particles of a normal soap type emulsion are shown in Fig. 11.

A rather pretty demonstration of the rigid character of the stabilizing clay films may be seen under the microscope if soap solution is added to a clay

emulsion, and the treated emulsion kept under observation over a sufficient period. The added soap displaces the clay from the bitumen/water interface, replacing the rigid clay film by a non-rigid stabilizing film of soap, and then, as a result of interfacial tension forces, the elongated bitumen particles are slowly drawn up into spherical globules.

As manufactured, the clay emulsions are thixotropic pastes containing 50–60 per cent. of bitumen. They are extremely stable to mechanical and chemical forces, and do not coagulate on drying until practically the whole of the water has been evaporated. The residual films obtained from the emulsions retain the clay emulsifier as a kind of skeleton structure, which prevents flowing of the bitumen under heat. A surprising resistance to flow can be developed, and it is possible to heat such a film until ignition of the bitumen occurs, without flow taking place. This property renders the emulsions particularly valuable for the application of anti-corrosive coatings to metal or other surfaces, and for the waterproofing of all kinds of structures.

Owing to their high stability, clay emulsions can be added directly to the paper pulp for the manufacture of bituminized paper, thus eliminating a second impregnating process, and they find a considerable application in the production of waterproof wrappings, carton boards, panel board, etc. In conjunction with cement, aggregates, and a variety of fillers, they provide mastics and waterproof compositions for roofing and flooring.

The space at our disposal does not permit of more than this very brief summary of the purposes for which bituminous emulsions are used, but sufficient has been said to indicate the wide field which has been opened up.

Conclusion.

The general purpose of this paper has been to show the progress of the bituminous emulsion industry and of the emulsions themselves, from the beginnings, which were purely empirical, to the position to-day, where it may be claimed that the industry is on a sound, scientific basis and the products are produced by precision-controlled methods. The emulsions, even in the early days, were found to have a wide field of utility, and the difficulties which had to be overcome were mainly those encountered in exceptional circumstances of application, or where the demands placed upon the finished products were exceptionally heavy. Owing to the increased knowledge of the constitution and behaviour of these emulsions, even these exceptional circumstances may now be dealt with with a great degree of success and, in fact, it may be said that bituminous emulsions are standardized to a degree certainly equal to that of any other product sold in equal bulk.

Concomitant with this development, a sound position has been built up in respect to specifications with which all products of this type are required to comply. The labile type of emulsion for surface-dressing and grouting is dealt with in British Standards Specification No. 434–1935 and this specification is specially noteworthy, in that it contains a first test for performance. This is the Lability Test, and although, in itself, the Lability Test is not a complete guide to performance, in that it deals only with the set of the emulsion due to evaporation and mechanical disturbance, never-

theless this is a good beginning. The bituminous emulsion industry has formed, from its principal members, the Road Emulsion and Cold Bituminous Roads Association, Ltd., and many of the technical advances which have taken place can be traced to the activities of the Technical Committee of that body. Technical co-operation between the various members of the industry is assured, thus providing the maximum degree of assistance and co-operation with the consumer, coupled with the beneficial effect of competition between the different manufacturers, to secure a satisfactory rate of technical and economic progress.

It is not often that it is possible to survey, in so limited a period, the growth from the very beginning to the fully equipped industry, of an industrial development of the degree of importance which has been assumed by the bituminous emulsion industry, and it is therefore hoped that the account which has been presented in this paper may be not only interesting to those in the industry, but also to the wider public constituted by the membership of the Institute of Petroleum.

The author is greatly indebted to his colleague, Mr. W. L. Peard, B.Sc., to whom much of the experimental work referred to is due, for his assistance in the preparation of this paper.

THE RELATIVE VOLATILITY OF PETROLEUM FRACTIONS.*

By R. Edgeworth-Johnstone, M.Sc., M.I.Chem.E., F.I.C.

In designing fractionating columns for complex mixtures by methods such as that of Underwood,[1, 2] it is necessary to know the relative volatility of adjacent narrow fractions. The relative volatility of two substances at any temperature is the ratio of their vapour pressures at that temperature. In the case of petroleum fractions, vapour pressures may be interpolated from a Cox or similar chart and the relative volatility thus calculated. Most vapour-pressure charts are based on data for pure hydrocarbons.

An empirical relation has been found whereby the relative volatility is obtained directly from the absolute temperature and the atmospheric boiling points of the components. Correlated on this basis the relative volatilities of pure hydrocarbons lie approximately on a single curve.

The relation is :—

$$\text{Log}_e \alpha = 11{\cdot}5 \frac{T_b^2 - T_a^2}{2T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or :

$$\text{Log}_{10} \alpha = 2{\cdot}50 \frac{T_b^2 - T_a^2}{T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where :—

α = relative volatility of component A with respect to component B at absolute temperature T,

T_a, T_b = absolute boiling-points of A and B at atmospheric pressure, T_a being the lower (in the case of narrow petroleum fractions, the average boiling points).

Temperatures may be expressed either in degrees Kelvin (Centigrade + 273) or Rankine (Fahrenheit + 460).

In arriving at this expression, relative volatilities were calculated for various combinations of twenty-one hydrocarbons, including normal paraffins, *iso*paraffins, *cyclo*paraffins, aromatics and a few olefins. Vapour pressures were taken from Rechenberg,[3] Perry [4] and the International Critical Tables. The lowest-boiling hydrocarbon included was propylene, b. p. −47° C.; the highest, hexadecane, b. p. 287·5° C. The pairs chosen consisted of hydrocarbons both of the same group and of different groups. The relative volatility of each pair was calculated at several temperatures. These ranged from temperatures corresponding to vapour pressures of 10–20 mm. up to or near the critical temperature of the lower-boiling component when data for the latter region were available.

The correlation obtained is shown in Fig. 1, in which log α is plotted against $(T_b^2 - T_a^2)/2T^2$. Ninety points are represented, although all are

* Paper received 19th May, 1939.

not visible, owing to overlapping. The greatest deviations from the average curve occur at very low vapour pressures, near the critical temperature, or at high values of the relative volatility.

At temperatures equal to or near the arithmetic mean of the atmospheric boiling points of the components $[(T_b + T_a)/2T = 1{\cdot}0]$, equation (1) reduces to the simpler form :

$$\text{Log}_e \alpha = 11{\cdot}5 \frac{T_b - T_a}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

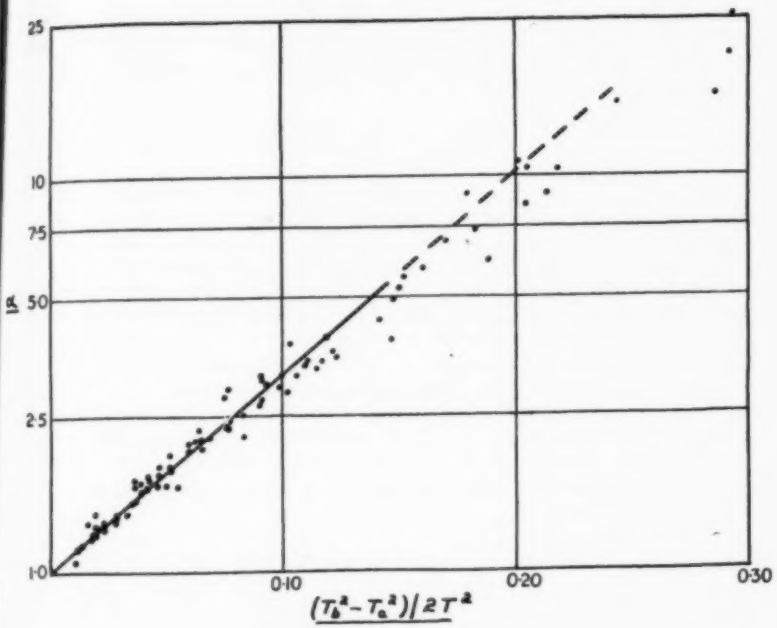

FIG. 1.

RELATIVE VOLATILITIES OF HYDROCARBONS.

This expression, with a slightly different constant, can be derived from the Clausius–Clapeyron equation and Trouton's rule.

Let :

P_a, P_b = Vapour pressure of components A and B at absolute temperature T.

M_a, M_b = Molecular weights of A and B.

L_a, L_b = Latent heats of vaporization of A and B at their respective boiling points.

R = Gas constant (heat units) = 1·986.

T_a, T_b, α are as defined above.

Integration of the Clausius–Clapeyron equation for component A, assuming constant molal heat of vaporization, gives :

$$\text{Log}_e P_a = \frac{M_a L_a}{R} \cdot \frac{T - T_a}{TT_a}$$

Combining this with Trouton's rule, $M_a L_a/T_a = 22$:

$$\text{Log}_e P_a = \frac{22}{R} \cdot \frac{T - T_a}{T}$$

A similar equation is obtained for component B. If it be assumed that the latent heats of vaporization remain substantially constant over the range of temperature from T_a to T_b, then the two equations may be combined, whence :

$$\text{Log}_e \frac{P_a}{P_b} = \frac{22}{R} \cdot \frac{T_b - T_a}{T}$$

or

$$\text{Log}_e \alpha = 11{\cdot}1 \frac{T_b - T_a}{T}$$

The assumption regarding constant latent heats of vaporization evidently cannot hold for temperatures far removed from the atmospheric boiling points of the components, and equation (3) is then considerably in error. To secure correlation under these conditions it was found necessary to introduce the empirical factor $(T_b + T_a)/2T$, giving equation (1).

In petroleum distillation calculations involving complex mixtures of hydrocarbons, the range of relative volatilities and vapour pressures is normally much less wide than that represented in Fig. 1. For narrow fractions it is believed that equation (1) or (2) will be found to give a satisfactory degree of approximation to the relative volatility under all practical conditions.

ACKNOWLEDGEMENT.

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AN ACCELERATED OXIDATION TEST FOR OILS.*

By W. Francis, M.Sc., Ph.D., F.I.C., and K. R. Garrett, B.Sc.

Summary.

The various modifications of the Michie sludging test that are in use for measuring the oxidizability of an oil are difficult and laborious methods. A new method for determining the oxidizability of oil is described, using a solution of alkaline potassium permanganate under standard conditions as oxidizing agent. The whole determination can be carried out in a few hours with a simple apparatus and the results obtained on a number of different types of oil appear to be capable of correlation with the behaviour of these oils in practice. Not only can the oxidizability of new oils be determined but the state of oxidation of an old oil can readily be ascertained by the new method. The experimental conditions can be modified to increase or decrease the severity of oxidation so as to discriminate more readily between oils of similar oxidizability at either end of the scale.

The authors have recently pointed out the unsatisfactory nature of the existing standard methods for the chemical examination of lubricating oils, particularly in their application to the measurement of the changes occurring in such oils under operating conditions. In an endeavour to improve matters it has been suggested that the standard methods should be modified, and followed by determining the oxidized groupings appearing in the oil during oxidation.

These methods are of value in measuring the effect of oxidation, and especially the rate of deterioration of oils in practice. It is, however, of greater advantage to be able to anticipate the course of events by the evaluation of the liability of oils to oxidation. The authors' attention has now been focused on the measurement of this property.

The oxidizability of oils is usually measured by the Michie test [2] or modifications of it. The general procedure is to pass air at a standard rate through a standard volume of oil in which is placed a strip of clean copper foil. The whole is maintained at a constant temperature, and the sludge formation, change in viscosity, or carbon residue is measured and assumed to give an indication of the tendency to sludge. In the standard tests of the B.E.I.R.A., the I.P.T. or the B.S.I. (*loc. cit.*) the rate of flow of air is two litres per hour, the temperature of the oil is 150° C., and the duration is 45 hr. The sludge formation is estimated by weighing the insoluble matter produced by the addition of petroleum spirit. In the British Air Ministry modification the rate of flow is 15 litres per hour, the temperature is 200° C. and the duration of heating two periods of 6 hr. on consecutive days. The increase in viscosity or carbon residue value before and after oxidation is taken as an index of the oxidizability of the oil.

It is apparent that these tests are difficult and tedious to carry out, and the errors in the determination of the extent of change in the oils are relatively large.

Because of the success obtained by one of the authors [3] in the parallel

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problem of determining the oxidizability of coal by means of its reactivity towards alkaline potassium permanganate solution under standard conditions, it was decided to explore the possibility of adapting this procedure to the determination of the oxidizability of oils. The problem differs from that of determining the reactivity of coal mainly because the available surface of interaction of a given weight of coal is determined by the size, shape, and uniformity of the coal particles, whereas with oil, which floats on the surface of alkaline permanganate, the available surface is the surface area of the aqueous solution. The rate of oxidation of oil depends on the weight of oil taken, its oxidizability, the interfacial area between the oil and alkaline permanganate, the temperature, the rate of diffusion of the oxidation products of the oil from the interfacial surface, and the concentration of alkaline permanganate at the interfacial surface. Since the authors are at the moment interested only in obtaining an index for the oxidizability of an oil, this can be done by fixing the factors arbitrarily in a manner capable of giving a significant reproducible numerical value to this property for the range of oils under examination.

After a preliminary investigation regarding the effect of the above factors on the results, three methods at different temperatures were tried out.

(1) Samples of a turbine oil after varying periods of service were taken and 10 gm. of each were weighed into standard sized 600 ml. beakers; 100 ml. of N-potassium permanganate (containing 31·8 gm. per litre) and 25 ml. of N-caustic soda were added. After allowing to stand for 72 hr. at laboratory temperature (approximately 20° C.), the contents were filtered under suction through a frittered glass filter (25.G.3). The filtrate was then warmed to 60° C., acidified with sulphuric acid, and titrated rapidly against N-oxalic acid in the usual manner. A blank test was carried out with permanganate and caustic soda alone under the above conditions.

(2) 10 gm. of each of the above oils were weighed into thin glass bulbs of capacity approximately 15 ml. Each bulb was broken by dropping it into a round-bottomed flask of capacity 4 litres: 50 ml. of N-caustic soda and 200 ml. of N-potassium permanganate were added. The flask was attached to a Liebig condenser, by means of a ground-glass joint, and the contents were boiled as quietly as possible for 50 min. The solution was filtered and titrated as in (1).

(3) 20 gm. of each of the above oils were weighed into standard-sized flat-bottomed litre flasks and 40 ml. of N-caustic soda added, followed by 150 ml. of N-potassium permanganate. Each flask was then placed on a boiling water-bath for 2 hr. The temperature of the solution during this period remained approximately constant at 95° C. The amount of permanganate used was estimated as above.

The results obtained by the above three methods are given in Table I.

The results are comparable, in that the oils are arranged in the same order of oxidizability. While it is considered that method (1) is the most accurate under our experimental conditions, the time taken is too long for a routine test. Method (2) gives significant results in the shortest time, and temperature control is simplified. Unfortunately, however, the reaction is violent with highly oxidizable oils, and severe bumping may alter the interacting surface area to an indeterminate amount.

Method (3) is a compromise, in that the reaction proceeds quietly, and so

ensures a constant interfacial surface, whilst the time required is considerably shortened compared with method (1) at atmospheric temperature. For extreme accuracy, of course, the temperature of the solution should be controlled by a thermostat at 95° C.

TABLE I.

Stage of Oxidation.	ml. of *N*-potassium permanganate used.		
	1. After standing for 76 hr. at laboratory temperature.	2. Boiling for 50 min.	3. Heating to 95° C. quiescently for 2 hr.
New Turbine Oil	0·5	2·4	2·3
1.	4·3	13·4	11·0
2.	11·9	35·0	13·6
3.	12·1	46·0	20·9
4.	14·8	47·9	28·3
5.	17·5	51·0	35·6

It is important to titrate as rapidly as possible, after acidifying the permanganate, because the acid permanganate is unstable in the presence of any remaining reducing matter left behind in highly oxidizable oils.

The authors advocate method (3) under controlled temperature conditions as a standard for normal lubricating and insulating oils. The number of mls. of normal permanganate used under these conditions is called the "permanganate number," and this is used as an index of oxidizability. To obtain this for extremely reactive oils, which would decompose all the permanganate under the standard conditions, less oil or more permanganate may be taken. It is sufficient, in such cases, to record the permanganate number as being greater than 150.

Table II contains the results of the examination of a number of oils by the standard method, and compares the permanganate number with the Ramsbottom coke test before and after oxidation by the Michie method.

As would be expected, the permanganate number decreases with increased refining. With highly refined mineral oils the permanganate number is about 2, and with oils from the same source, but not so highly refined, about 16. Vegetable oils decompose all the permanganate, being more reactive and more liable to sludge than mineral lubricating or insulating oils.

It is interesting to observe that some of the products produced by the deterioration of turbine oils in practice are much more oxidizable than the oils themselves. Thus, some of the solid sludge removed from a centrifuge used to clarify such oils, reacted so readily with alkaline permanganate under standard conditions that all the permanganate was used up before the end of the experiment. On repeating, using only 1 gm. of sludge, 72 ml. of permanganate were decomposed. Moreover, some of the oxidation products removed by alcoholic extraction from a used oil, of acidity 425 mgm. KOH/100 gm. oil and permanganate number 120, were remarkably reactive towards permanganate. Under standard conditions of oxidation, but using 0·1 gm. of this resinous material, 85 ml. of permanganate were decomposed. The permanganate number of the extracted oil was only

TABLE II.

Oil.	Description.	Permanganate no.	Ramsbottom.	
			Before oxidation.	After oxidation.
Olive oil.	Vegetable oil, high sludging properties.	>150		
Castor oil.	Vegetable oil, high sludging properties.	>150		
Low-grade American.	Light straight mineral oil used for diluting cutting oils and flushing.	17·1	0·33	3·4
Low-grade American coastal.	Medium oil used for bearings and machinery.	15·0		
Low-grade American.	General purpose heavy lubricating oil.	14·2	0·33	3·4
Mid-continent American dewaxed.	General purpose lubricating oil and turbines.	3·0	0·13	1·8
South American, highly refined by selective solvent process.	Low sludging properties. Cylinder, gearboxes, etc.	2·9	0·17	0·77
American high-grade, selective solvent process.	Turbines, bearings, etc.	2·7	0·11	1·17
Mid-continent American, highly refined, distilled and acid treatment.	Turbines, general lubrication.	2·3	0·14	1·3
American high-grade.	Hydraulic couplings, etc.	1·9	0·11	1·28
Transformer, Naphthene base.	Grade A.30.	1·3		
Transformer, Naphthene base.	Grade B.30.	2·5		
Transformer, Naphthene base.	Grade B.0.	4·8		

14·6, showing that the alcohol-soluble products were responsible for the bulk of the reaction with permanganate. Consequently, if all the oxidation products obtained in service remain in an oil, the determination of the permanganate number appears to be a measure of the degree of oxidation that has occurred.

Unfortunately, from the point of view of checking this point, normal practice is to remove sludge or emulsions from turbine oils by the regular use of a centrifuge. Water-soluble products are constantly being removed from the system, and if the rate of removal of insoluble products is greater than the rate of formation, the permanganate number of the residual oil

will not rise after equilibrium has been reached, and it may even fall. This is, in fact, what has occurred with the turbine oils shown in Table III.

TABLE III.

Approx. no. of months in service.	Permanganate no.	ml. of gas at N.T.P. liberated by Grignard reagent.	Acidity, mgms. KOH/100 gm. oil.
0	2·3	2·0	0
4	11·0	9·7	8·9
7	13·6	12·8	15·9
9	20·9	17·7	34·7
11	24·7	21·0	45·3
15	27·3	22·4	64·9
19	33·7	24·4	71·1
22	35·6	24·1	71·1
29	31·1	21·5	65·0

The permanganate number, reactivity towards Grignard reagent, and acidity are compared over a period of 29 months in service. During the first nineteen months the values of all three increased correspondingly, and then remained fairly constant for the next three months. After this period a slight decrease in all three occurred over a period of seven months.

The behaviour of a highly refined oil, containing an inhibitor, is also of interest. The new oil gave a permanganate number of 4·4, the inhibitor itself being mainly responsible for this small reactivity. After three years service the permanganate number was only 4·1, which suggests that little oxidation had occurred, but that some of the inhibitor had been lost. This is confirmed by the Grignard reaction,[1] in which the amount of gas liberated from the new oil was 2·3 ml. and from the used oil 1·3 ml. The appearance and usual tests on the oil confirmed the absence of any marked degree of oxidation; the acidity, for example, only reaching the value of 5 mgm. KOH/100 gm. oil during this period.

The authors feel justified in concluding that the standard method described above gives a measure not only of the relative oxidizability of new oils, but also the extent to which an oil has deteriorated in service. It is offered as an additional method for the examination of oils in the hope that it will be helpful where further evidence on oxidation is required or where a rapid determination of oxidizability is desired.

References.

[1] W. Francis and K. R. Garrett, *J. Instn. Petrol. Tech.*, 1938, **24** (178), 435.
[2] B.S.S. No. 148.
[3] W. Francis, *Fuel*, 1933, 128.

A NEW LABORATORY METHOD FOR RATING AVIATION FUELS OF HIGH OCTANE NUMBER.

By R. Stansfield, A.M.Inst.C.E., M.Inst.Pet., and H. B. Taylor, A.F.R.Ae.S.

It has been recognized for some years that laboratory ratings of aviation fuels are unsatisfactory with existing equipment and technique, and many attempts have been made to improve correlation with aero-engine behaviour. The problem has been complicated because of lack of really satisfactory means for examining full-scale performance as regards detonation, and opinion differs sharply on the relative merits of various proposals for full-scale knock testing, upon the results of which any laboratory test must be based.

The first tentative standard method adopted for fuels to meet British Air Ministry specifications was the outcome of tests in single-cylinder aero-engine units, knock being determined under conditions of maximum economy and for fuels of lower octane number than now prevail. The laboratory method based on these results depended on the use of the C.F.R. engine running under Motor Method conditions, except that the mixture temperature was adjusted to 260° F. instead of 300°. As the use of 87 and 100 octane-number fuels became more important it was found that an increase of mixture temperature to the Motor Method value was desirable, and alteration to this method has recently been recommended by the Knock Rating Panel of the Institute of Petroleum.

This change is not considered to be a complete answer to the correlation problem, as it is known that fuels of equal knock rating under cruising conditions may differ considerably when the engine is running under more highly supercharged and rich-mixture take-off conditions where mixture strength is used for limiting detonation.

It is not intended here to give a complete summary of the several proposals for improved ratings, but it is notable that practically every attempt has been influenced by the assumption that lack of correlation with the C.F.R. engine is due very largely to the great dissimilarity between this unit and an aero-engine cylinder. Thus the test engine has been modified by altering cylinder dimensions to permit an aluminium piston to be used at high rotational speeds, with or without increase of jacket temperature; supercharging has been provided for, and the valve system and carburettor have been altered to give greater breathing capacity; the bouncing pin has been replaced by a temperature plug, or a piezo-electric indicating unit, and even audibility methods have been used according to the ideas of the experimenters concerned. British and some Continental work has been influenced largely by the results of single-cylinder aero-engine tests under rich-mixture conditions, while American developments appear to be directed more by full-scale engine tests in which the temperature rise of suitably placed thermocouples is assumed to be the criterion of failure, although pre-ignition and other factors have also received attention.

The development work leading to the method to be suggested is based

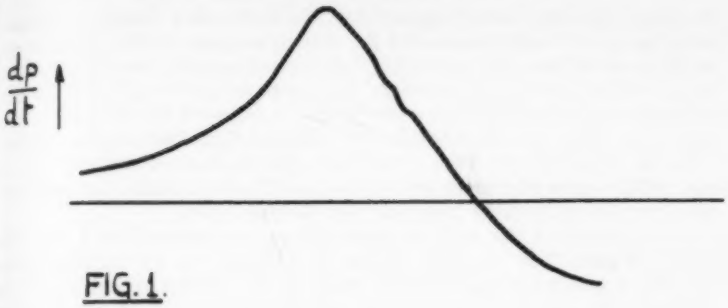

FIG. 1.

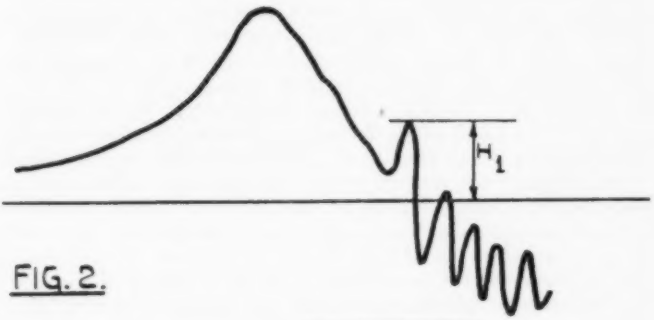

FIG. 2.

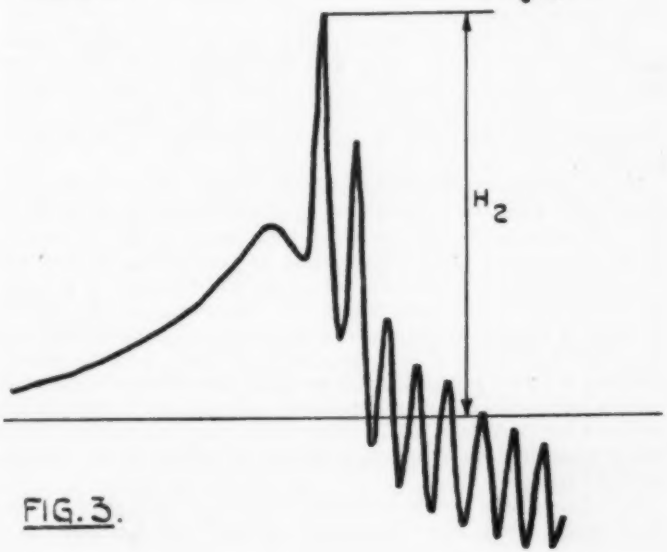

FIG. 3.

on two premises: first, that any fuel must exceed a definite minimum anti-knock value appropriate for its class when used under lean-mixture cruising conditions, and, secondly, that it must exceed a second minimum when used under rich mixture conditions appropriate for take-off, the two minima not necessarily being the same in terms of the reference fuels adopted. Only data from a full-scale British-designed aero engine of large cylinder capacity have been considered, but there does not seem to be any valid reason why more than minor modifications should be needed to give correlation for other important aero-engine types.

Development of the method started from two assumptions: that the Motor Method, itself a weak-mixture test and, so far as our present information goes, agreeing with aero-engine weak-mixture ratings, should be fairly readily capable of alteration to suit rich-mixture conditions, and that instrumentation, such as provided by the bouncing pin, the temperature plug, or oscillograph pressure diagrams, was unsuitable. The latter assumptions were made as a result of a series of instrumentation tests carried out some two years ago in connection with the rating of motor fuels. Figs. 1, 2 and 3 are reproductions of oscillographs showing the rate of change of pressure in a C.F.R. engine under smooth running, light knock, and heavy knock conditions, respectively. The bouncing pin cannot respond to the knock of Fig. 2, because the rate of pressure rise of the general combustion is greater than that of the knock effect at the point of measurement. It may not respond even to the knock of Fig. 3 if the engine is being run at a high compression ratio, because then the pre-knock rate of pressure rise may be great enough to throw the pin away from control of the diaphragm before the knock itself takes place. This does not mean that reproducible ratings cannot be obtained, but they will be influenced by the general combustion process before the knock, and not by the knock itself, and will therefore often be false.

These and other considerations led to the decision to use a cathode-ray oscillograph and an indicating unit showing rate of change of pressure diagrams, and to take as the measure of knock the height of the first wave of the detonation, the maximum observed height in a minute being recorded, and the mean of three such observations giving the required knock intensity.

Since absolute height of the detonation wave on the oscillogram can be affected by very small alterations to engine condition, even though compression ratio, mixture temperature, mixture strength, and running speed be held constant, the usual method of comparison against secondary standard fuel blends has been adopted. For example, if a series of 87-octane-number fuels is being tested, each fuel is compared for peak height of detonation wave with the height given under identical running conditions by a blend of C and F secondary reference fuels, and the rating is first given as a knock ratio. Thus if an 87-octane-number blend of C and F gives a height of 3 in. and a sample a height of 2 in., the sample is rated as having a knock ratio of 0·67. These ratios may be converted into equivalent octane numbers by testing a series of C and F blends which cover the required range.

Fig. 4 shows the results of a comprehensive set of tests made on several fuels ranging from 87 to 91 octane number Motor Method, and the full-

scale behaviour of which was known in an important design of air-cooled engine under both weak- and rich-mixture conditions. Considering the curve for fuel A, this sample was run through a jet-type flow-meter to the

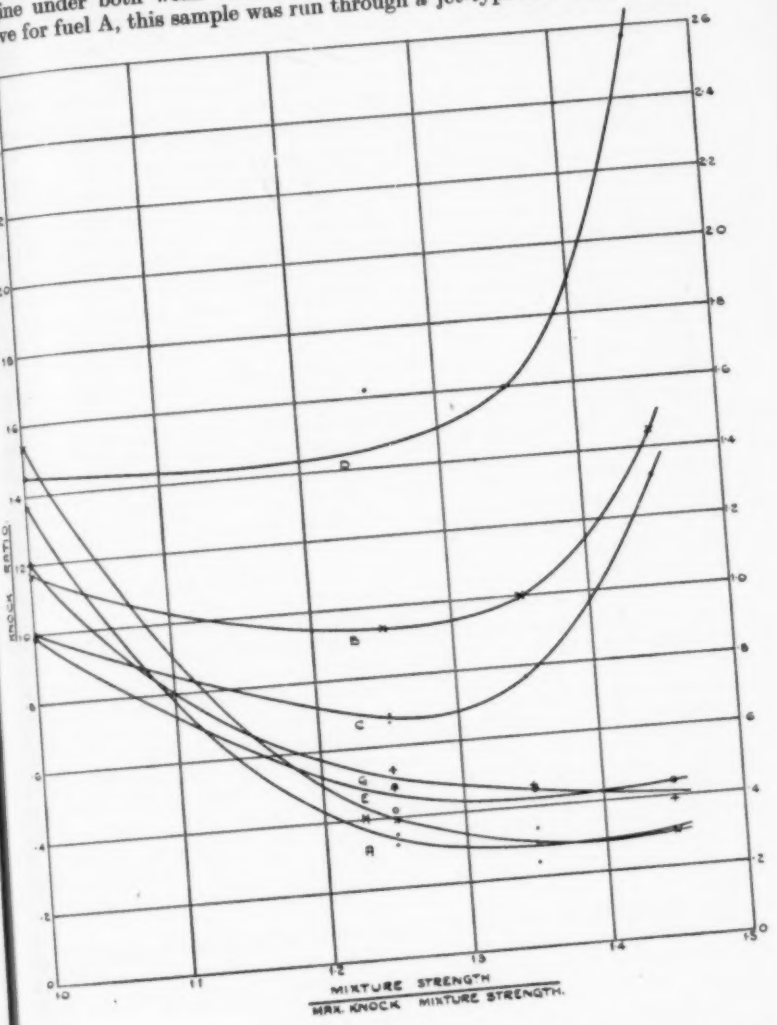

FIG. 4.

C.F.R. engine, and the mixture strength adjusted to give maximum knock as measured by the height of the detonation wave of the oscillogram. The mixture temperature was maintained at 300° F. and the speed at 900 r.p.m., as for Motor Method testing. The compression ratio was adjusted

so that the detonation wave was about the same height as that of the pre-knock pressure rise, although the setting is not critical. After determining the mean of three separate observations of the maxima occurring in a minute, a similar test was made on a 91·0-octane-number blend of C and F. The height ratio was 1·35, which is the starting point of the curve for fuel A. The other samples were all tested similarly against 91·0-octane-number reference blend, and it was found that the knock-ratio ratings agreed in order very closely with the Motor Method ratings, and they are therefore appropriate for the aero engine under weak-mixture conditions.

The fuel flows for maximum knock were recorded and a mean value was determined for all the fuels. From this mean value were calculated the flow-meter readings required to give 25 per cent., 35 per cent. and 45 per cent. rich mixtures, the richness figures being nominal in so far as no account was taken of possible small changes of volumetric efficiency under the rich-mixture test conditions. The fuel flows were made equal by volume, as this was found to give slightly better agreement than control on a weight basis.

Each fuel was then tested in comparison with the 91·0-octane-number blend of C and F at the 25 per cent. rich mixture, the compression ratio being raised to obtain about the same height of detonation wave for the C and F blend as used for the weak-mixture tests. Some of the fuels depreciated, whilst others appreciated, and tests at the still richer mixture further spread the relative ratings. At 45 per cent. rich the compression ratio for the poorer fuels had to be kept below that used for the better fuels, to prevent unduly heavy knocking. It was established, however, that relative ratings were not affected by the necessary small alterations of ratio, and thus the working conditions are not critical.

A test of one fuel at 55 per cent. rich resulted in a marked increase of knock ratio. It was noted that running was then very erratic, and it is probable that a state of incipient pre-ignition had been reached, possibly one which could have been alleviated by reduction of knock intensity. Investigation of this aspect of the method has not been completed, as it occurs beyond the mixture strength required for correlation.

Although the Motor Method octane numbers of the samples tested varied only between about 87 and 91, the spread under the 45 per cent. rich conditions was about 15 octane numbers as determined by tests on appropriate blends of C and F at this strength. The knock ratio depends, of course, on the secondary reference fuels used, "C" and tetraethyl lead giving entirely different ratios, but rating all fuels in relatively the same order.

Fig. 5 shows the knock ratios at 45 per cent. rich plotted against ratings made on the aero engine under take-off conditions, and agreement is within the accuracy of the aero engine tests themselves. Ratios for 40 per cent. are indicated by the dotted line.

The samples examined include paraffinic, naphthenic, and aromatic types, all with T.E.L. in amounts varying from 2½ to 4 ml. per Imp. Gall.

Should further work confirm the suitability of this type of test, the specification for knock testing of an aviation fuel would include a minimum octane number blend of specified secondary reference fuels which it must match under weak-mixture conditions, and a second minimum number for

a match at, say, 45 per cent. rich. Weak-mixture ratings could probably be determined better by rating at a definite engine power drop below optimum, rather than at a rather flatly defined maximum knock, although such

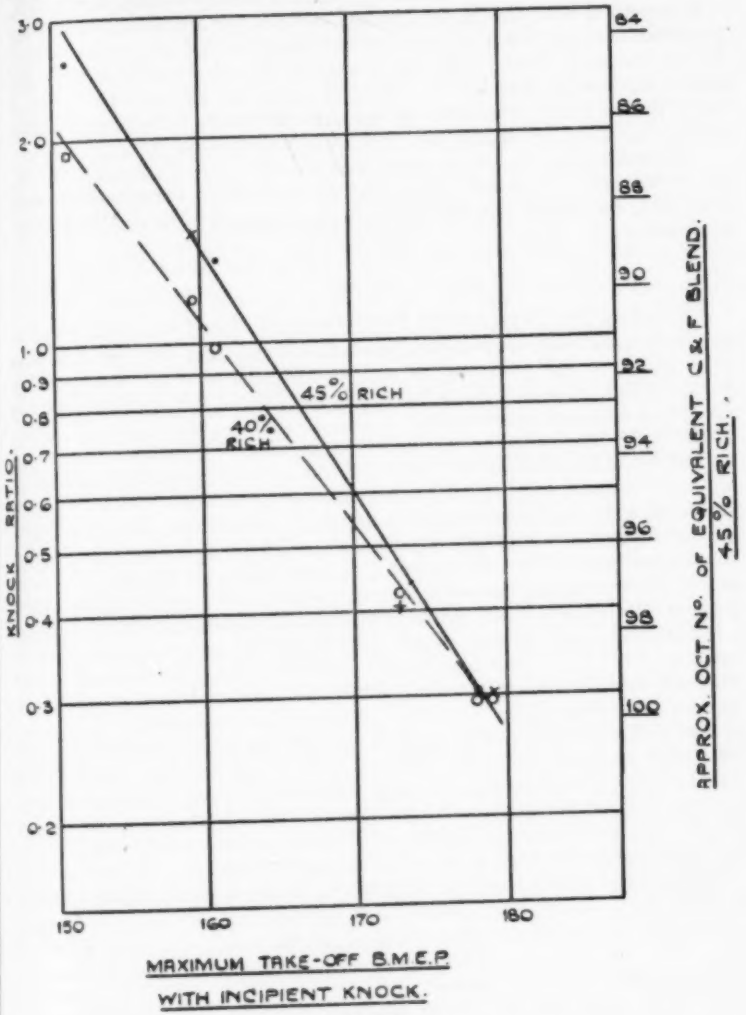

Fig. 5.

a technique requires a dynamometer for load absorption, or the use of a D.C. generator with which the speed falls with fall of engine output.

For the examples given in Fig. 4 the specification might be " not less

than 87 octane weak " and " not less than 95 octane at 45 per cent. rich," the latter corresponding to a knock ratio of not more than 0·55 in terms of the 91-octane blend of C and F under the test conditions from which Fig. 4 was obtained. Such a specification would be met by fuels A, E, G and H.

In common with the Motor Method of tests for automobile fuels, the proposed method is not assumed to reproduce actual engine conditions. It is a laboratory device which makes use of an existing engine with only simple modifications and easily obtained instrumentation, and no claim is made that it can be extended further than to obtain suitable correlation with aero-engine fuel ratings under cruising and take-off conditions.

The authors wish to thank the Chairman of the Anglo-Iranian Oil Co. for permission to publish the results of the C.F.R. experimental work described, and which was carried out in the Company's research laboratory at Sunbury.

Note.

Since the above was written further research has been carried out in connection with the method described, and correlation between rich mixture ratings on full scale engines and the rich mixture C.F.R. ratings has been shown to exist for 100 octane fuels with about the same accuracy as for the 87 octane number range.

The C.F.R. engine has been adjusted to run with a 19° fixed spark advance and with the inlet air heated to 150° F. the mixture being then heated in the usual manner to give a mixture temperature of 300° F. on a reference fuel under the appropriate mixture strength conditions, the heat input required for this being maintained constant for all fuels tested under the same conditions. The carburettor has been modified, the throttle plate being removed and a properly shaped venturi added which includes the jet and which gives about the same volumetric efficiency as when running without venturi or throttle plate. The flowmeter system and adjustable orifice control have been redesigned. The shrouded inlet valve has been retained as it improves stability, while the unshrouded valve gives no greater test range.

Modified as described, the engine is suitable for testing fuels at mixture strengths up to 45% rich at least up to the equivalent of F plus 2 ml. T.E.L./Imp. gal. without supercharge. Recent ratings have been expressed in terms of the matching blend of C and F with 2 ml. T.E.L./Imp. gal. required to give the same height of detonation wave on the oscillogram as the sample when used at the same mixture strength. This selection of reference fuels covers the entire commercial range from 87 octane number upwards.